









TRANSACTIONS  
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AND METALLURGICAL ENGINEERS  
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## PREFACE

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IN THIS volume are the papers and discussions presented at the New York Meeting, February, 1924, and at the Meeting of the Petroleum Division held in Tulsa, Okla., in October, 1923; also the Proceedings of the New York Meeting.



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 \*MCNAB, S. M., '71, '82.  
 \*MERRELL, CHARLES W., D. '14-16; V. '24  
 \*METCALF, WILLIAM, V. '78-9; P. '81.  
 \*MILLER, WILLET G., C. '09-11; D. '17-19.  
 \*MORRIS, PHILIP W., V. '02-4.  
 \*MOFFAT, E. S., M. '83, '85; V. '87, '89.  
 \*MOORE, PHILIP N., V. '15-16; P. '17, D. '18, '19  
 MUDD, S. W., V. '20-22; D. '23, '24.  
 \*MUNROE, H. S., M. '81-4; V. '90-1.  
 \*NEILL, JAMES W., M. '02-4.  
 \*NEILSON, W. G., M. '86-8.  
 \*NEVERREY, J. S., M. '76-8.  
 \*NORRIS, R. V., C. '08-10; V. '11-12, D. '20-24.  
 OLCOTT, E. E., P. '01-2.  
 OLCOTT, W. J., M. '98-00; C. '11-12; D. '13.  
 PAGE, W. N., V. '99-00.  
 PARKER, E. W., M. '02-4.  
 \*PARSON, RICHARD, V. '85-6; P. '89.  
 \*PARSON, JOHN B., V. '77-8.  
 \*PECKIN, E. C., M. '73, '75-6, '85, '91-2  
 \*PETERS, E. D., Jr., V. '98-9.  
 \*PETERKIRK, THOMAS, M. '71-2; V. '84.  
 \*PETTER, WM. H., M. '73, '89-91; V. '81-2  
 \*PLATT, J. C., V. '94-5.  
 PORTER, J. A., M. '91-3.  
 POTTER, E. C., V. '99-00.  
 \*POTTER, WILLIAM B., M. '78-80; P. '88.  
 POWELL, J. W., V. '82-3.  
 PRIDE, FRED, JR., M. '71-3.  
 \*PUMPELLY, RAFAEL, M. '71.  
 QUARRIE, BERTRAM D., D. '24.



- \*RALSTON, W. C., V, '00-1, '09-10.  
 RAND, CHARLES F., C, '10-12, D, '12; '16-24;  
 F, '13; T, '22-24.  
 \*RAND, THEODORE D., T, '73-02.  
 \*RANDOL, J. B., V, '00-1.  
 RANDOLPH, J. C. F., M, '81-3; V, '91-2.  
 \*RAYMOND, ROBERT M., D, '17-18; V, '18-20.  
 \*RAYMOND, R. W., V, '71, '78-7; P, '72-4; S, '84-  
 11; S. Em. '11-18.  
 REGUA, MARK L., V, '17-19.  
 REYNOLDS, J. V. W., D, '19-21; V, '22-24.  
 \*RICHARDS, JOSEPH W., V, '10-11; C, '12; D,  
 '13-15; V, '16-17.  
 RICHARDS, ROBERT H., V, '79-80; P, '86.  
 RICKARD, T. A., M, '84-6; D, '05; C, '05-6.  
 RICKETTS, L. D., D, '13-18; P, '16; D, '19.  
 RIES, HEINRICH, M, '03-4; C, '08.  
 ROBERTS, PERCIVAL, JR., M, '80-2; V, '89-90.  
 ROBERTSON, KENNETH, M, '88-90.  
 ROBERTSON, WM. F., C, '06-8.  
 ROBINSON, BURN A., S, '13-17.  
 ROBINSON, C. S., D, '13.  
 ROGERS, ALLEN H., D, '17-19.  
 ROLKER, C. M., M, '88-90.  
 \*ROTHERWELL, RICHARD P., M, '71, '88-00; V,  
 '72-3, '75-6; P, '82.  
 SALES, RENO H., D, '23-24.  
 SAUNDERS, W. L., V, '09-10, '14; P, '15; D,  
 '16, '17.  
 SAUVAGE, ALBERT, V, '10, '11.  
 SHARPLESS, FREDERICK F., S, '21-24; E, '21-23.  
 SHEAFER, W. L., M, '93-5.  
 \*SHINN, WILLIAM P., V, '77-8; P, '80.  
 SHOCKLEY, WILLIAM H., C, '08-10.  
 SHOOK, A. M., M, '93-5.  
 SMITH, FRANK M., V, '23-24.  
 SMITH, GEORGE OTIS, D, '21-24.  
 SMOCK, JOHN C., M, '75-7, '91-3.  
 SMYTH, HENRY L., D, '14-16.  
 SNOW, CHAS. H., M, '04; C, '05-8; D, '05-10.  
 \*SPILLBURY, E. G., M, '85-7; V, '93-4; P, '96.  
 \*STANTON, F. McM., M, '97-9.  
 \*STANTON, JOHN, V, '92-3.  
 \*STEARNS, I. A., V, '05-6.  
 \*STEARNS, T. B., D, '16-18, '22-24.  
 \*STETTERFELDT, C. A., V, '85-6, '95-6.  
 STONE, G. C., SD, '12; D, '13-19; T, '13-18.  
 STOUGHTON, BRADLEY, S. E., '13-21.  
 \*STREUTHERS, J., S, '03-5; S, '06-10; t, E, '06-12;  
 D, '11; S, '11-12.  
 \*SWOTER, J. H., V, '71.  
 \*SYMONS, W. R., V, '71-2; M, '73-4.  
 TAYLOR, SAMUEL A., D, '15-20.  
 \*TAYLOR, W. J., M, '90-2, '99-01.  
 TRACER, ARTHUR, D, '18-20.  
 TRAYER, BENJAMIN B., V, '12-13, '24; P, '14;  
 D, '17-18.  
 \*THOMAS, DAVID, P, '71.  
 \*THOMAS, SAMUEL, V, '79-80.  
 \*THOMPSON, CHARLES O., V, '81-2.  
 \*THURSTON, ROBERT H., V, '78-9.  
 \*VALENTINE, M. D., M, '02-4.  
 WALCOTT, C. D., V, '04-5.  
 WALKER, ARTHUR L., D, '11.  
 \*WALKER, W. R., D, '19.  
 WEBSTER, WILLIAM R., M, '95-7.  
 \*WEEKS, J. D., V, '86-7; M, '90-2; P, '95.  
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 \*WILLIAMS, GARDNER F., V, '11-12.  
 WILLIAMS, T. M., M, '71.  
 \*WILLIAMSON, J. FRYOR, T, '71-2.  
 \*WINCHELL, H. V., M, '01-3; V, '09-10; P, '19;  
 D, '20, '21.  
 WINSLOW, A., M, '99-01.  
 \*WITHERBEE, THOS. F., M, '76-8.  
 WOOD, WALTER, C, '06-8.  
 WRATNER, W. E., D, '21-23.  
 \*YOUNG, EDWARD L., C, '11-12; D, '13-14.

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\*Deceased.

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1922.	FEDERICO GIOLITTI.....	Torino, Italy.
1888.	HATON DE LA GOUFILLIERE.....	Paris, France.
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1917.	HERBERT HOOVER.....	Washington, D. C.
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1872.	SIR LOWTHIAN BELL.....1904	1886.	JOHN PERCY.....1889
1905.	ANDREW CAENEGIE.....1919	1888.	FRANZ POSEFNY.....1895
1892.	A. DEL CASTILLO.....1895	1911.	ROSSITER W. RAYMOND.....1918
1902.	MANUEL MARIA CONTRERAS 1902	1884.	THEODOR RICHTER.....1898
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1906.	JAMES DOUGLAS.....1918	1890.	ALBERT SERLO.....1898
1884.	THOMAS M. DROWN.....1904	1880.	C. WILLIAM SIEMENS.....1883
1890.	MORITZ GAETZSCHMANN.....1895	1906.	JOHN E. STEAD.....1923
1873.	L. GRUNER.....1883	1909.	JAMES M. SWANK.....1914
1921.	HEINRICH O. HOFMAN.....1924	1872.	DAVID THOMAS.....1882
1919.	ROBERT W. HUNT. ....1923	1902.	DIMITRY CONSTANTIN
1891.	BRUNO KERL.....1905		TSCHERNOFF.....1921
1895.	JOSEPH LE CONTE.....1901	1873.	PETER R. VON TUNNER.....1897
1891.	J. P. LESLEY.....1903	1885.	HERMANN WEDDING.....1908
1899.	FLORIS OSMOND.....1912	1910.	TSUNASHIRO WADA.....1920

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(In coöperation with Woman's Auxiliary)

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GEORGE D. BARRON

ARTHUR S. DWIGHT

<sup>1</sup> Until Feb., 1925.<sup>2</sup> Until Feb., 1926.<sup>3</sup> Until Feb., 1927.<sup>4</sup> Until Feb., 1928.

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 F. M. MINISTER SELDEN S. RODGERS

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<i>Executive Committee</i>		
H. FOSTER BAIN	FREDERICK J. BAILEY*	SAMUEL GOMPERS
DAVID T. DAY		JOHN L. LEWIS
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	Mining and Quarrying Industries	
ROBERT LINTON	EDGAR WALLACE	J. W. PAUL
	Metallurgical and Other Industries	
G. H. CLEVINGER	JOHN TURNEY	VAN H. MANNING

## Washington Award Commission

W. L. ABBOTT,§ <i>Chairman</i>	EDGAR S. NETHERCUT, <i>Secretary</i>
CHARLES H. MacDOWELL*	HERBERT S. PHILBRICK†
F. K. COPELAND*	CHARLES F. BRUSH†
JOHN PRICE JACKSON†	CHARLES R. RICHARDS†
CHARLES F. SCOTT†	D. H. MAURY‡
R. C. MARSHALL, JR.‡	JOHN F. HAYWARD‡
W. H. FINLEY‡	C. A. MORSE‡
	H. J. BURT‡
	J. L. HECHT‡
	W. W. DUBERARD‡
	H. H. CLARK‡
	E. T. HOWSON‡

## Franco-American Engineering Committee

(Organized 1919 to foster engineering relations between France and America)

GEORGE F. SWAIN‡	NELSON P. LEWIS,¹‡ <i>Chairman</i>	LEWIS B. STILLWELL†
F. G. COTTRELL*	ARTHUR S. DWIGHT*	A. M. HUNT†
	CHARLES T. MAIN†	
	GEORGE W. FULLER†	

## American Bureau of Welding

*A. I. M. E. Representative*

BRADLEY STOUGHTON

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\*A. I. M. E.    †A. S. M. E.    ‡A. I. E. E.    §A. S. C. E.    §Western Soc. Engrs.  
 ¹Deceased



# PROCEEDINGS





## New York Meeting, 1924

THE 129th meeting of the American Institute of Mining and Metallurgical Engineers convened at New York City, in the Engineering Societies Building, Feb. 18-20, 1924. On February 21 an excursion was made to the Bethlehem Steel Co., at Bethlehem, where about 200 members and guests were splendidly entertained. The meeting and excursion were largely attended; the registration at New York totaled 1276 versus 1201 in 1923.

William Kelly, long identified with the iron-mining industry of the Lake Superior district, was elected President of the A. I. M. E. for the coming year, at the annual business meeting, Feb. 19, succeeding E. P. Mathewson. The following Directors were also elected (the date signifies year of termination of office; the final figure indicates the "District" the Director represents).

William Kelly, *Director* (1927-5).

B. B. Thayer, *Director* (1925-0).

Charles W. Merrill, *Director and Vice-president* (1927-10).

P. B. Butler, *Director* (1927-8).

Bertram D. Quarrie, *Director* (1927-3).

L. D. Ricketts, *Director* (1927-9).

J. V. W. Reynders was re-elected First Vice-president; Charles F. Rand, Treasurer; F. F. Sharpless, Secretary; and Percy E. Barbour, Assistant Secretary, at the executive session following the election of the new officials on Tuesday evening.

## SPECIAL LECTURES

Dr. Zay Jeffries delivered the annual lecture for the Institute of Metals Division. The examination by  $x$ -rays of the crystal structure of metals has been a special field of investigation for four years past by Doctor Jeffries. The results of those  $x$ -ray studies were embodied, in part, in the lecture, "The Trend in the Science of Metals."

An interesting coincidence marks the selection of Dr. Albert Sauveur to deliver the first H. M. Howe Memorial Lecture before the American Institute of Mining and Metallurgical Engineers. After the selection was made, Doctor Sauveur was honored by the Iron and Steel Institute of Great Britain with the award of the Bessemer medal for 1924 to be presented at the May meeting of the British Institute in London. The American metallurgist last honored in this way was Henry Marion Howe, 29 years ago. Doctors Howe and Sauveur were intimate friends and co-workers. The award of the Bessemer medal for 1924 carries special emphasis, as this is the semi-centennial of its

founding in 1874. Prior to Doctor Howe in 1895, only four Americans won the honor: Peter Cooper in 1879, Alexander Lyman Holley in 1882, Abram S. Hewitt in 1890 and John Fritz in 1893. The last three (as also Doctor Howe) were all presidents of the A. I. M. E.; Holley in 1875, Hewitt in 1876 and 1890; Howe in 1893, and Fritz in 1894.

### TECHNICAL SESSIONS

Joint sessions with the members and guests of the Institute were held by the following societies and committees: Advisory Board to Bureau of Mines and Bureau of Standards (Committee on Drill Steel); American Society for Testing Materials (Committee B-2 on Non-ferrous Metals); Institute of Metals Division; Mining and Metallurgical Society of America; National Research Council (Committee on Heat Treatment of Carbon Steel); National Safety Council (Mining Section); Society of Economic Geologists.

Besides the technical papers on special or individual fields of mining, milling, and metallurgic practice, and mineral and metal production, a number of programs of general engineering and general public interest specially enlivened the sessions.

A symposium on petroleum and gas developments in 1923 attracted much general attention; as did a symposium by the geologists on the nature of secondary enrichment in the genesis of copper orebodies, and one by metallurgists on the use of oxygenated air in furnaces; a timber and reforestation round-table (a subject in which both coal and metal mines have a common interest with the lumber and paper-pulp trades); a conference on taxation under the chairmanship of Paul Armitage, which drew attention in the public press; as did also several conferences on industrial relations between employers and superintendents and other workers.

### *Petroleum*

MONDAY MORNING, FEB. 18

Chairman, E. DeGolyer

Preparation of Composite Decline Curves of Oil or Gas Wells from Trade Journal Data or Scout Reports, ROSWELL H. JOHNSON, *Professor of Oil and Gas Production, University of Pittsburgh, Pittsburgh, Pa.*, and CHARLES L. SHIRLEY.

Distribution of Profit and Risk between Oil Land Owner and Producer. ROSWELL H. JOHNSON.

Smackover Oil Field. H. G. SCHNEIDER, *Division Geologist, Amerada Petroleum Corpn., Shreveport, La.*

Production and Water Conditions of the Powell Field, Texas. F. W. DEWOLF, *Chief Geologist of Boyd Oil Co.*, and R. B. WHITEHEAD, *Chief Geologist of Atlantic Oil Producing Co., Dallas, Texas.*

The Law of Supply and Demand. ARTHUR KNAPP, *Philadelphia, Pa.*

The Trend of Prices in the Petroleum Industry. JOSEPH E. FOGUE, *Consulting Engineer, New York City.*

*Developments during 1923*

Chairman, E. DeGolyer

## MONDAY AFTERNOON

Production of Petroleum in 1923. E. DEGOLYER, *Petroleum Geologist*, New York, N. Y.  
California. E. G. GAYLORD and L. C. DECIUS, *Pacific Oil Co.*, San Francisco, Calif.  
Rocky Mountain States. C. A. FISHER, *Consulting Geologist*, Denver, Colo.  
Kansas. J. M. SANDS, *Phillips Petroleum Co.*, Bartlesville, Okla.  
Oklahoma. JAMES H. GARDNER, *President, Gardner Petroleum Co.*, Tulsa, Okla.  
East Central Texas. F. JULIUS FOHS, *Consulting Oil Geologist*, New York.  
Gulf Coast (Louisiana and Texas). EDWIN T. DUMBLE and W. F. BOWMAN, *Southern Pacific Railway Co.*, Houston, Texas.  
Northern Louisiana and Southern Arkansas. MALCOLM E. WILSON, *Chief Geologist, Louisiana Oil Corpn.*, Shreveport, La.  
Illinois. JAMES H. HANCE, *Asst. Chief, Illinois State Geological Survey*, Urbana, Ill.

## TUESDAY MORNING, FEB. 19

Indiana. W. N. LOGAN, *State Geologist*, Indianapolis, Ind.  
Trenton Limestone of Northwestern Ohio. J. A. BOWNOCKER, *State Geologist*, Columbus, Ohio.  
Kentucky and Tennessee. WILBUR A. NELSON, *State Geologist*, Nashville, Tenn.  
Northern Appalachian Fields (Pennsylvania and New York). GEORGE H. ASHLEY, *State Geologist*, Harrisburg, Pa.  
Southern Appalachian Fields (West Virginia). DAVID B. REGER, *Assistant Geologist, West Virginia Geological Survey*, Morgantown, W. Va.  
Recent Deep Drilling in the Appalachian Fields. R. E. SOMERS, *Professor of Economic Geology, University of Pittsburgh*, Pittsburgh, Pa.  
Oil Developments in the United States Outside of the Producing Oil States. K. C. HEALD, *Associate Geologist, U. S. Geological Survey*, Washington, D. C.  
Alaska. ALFRED H. BROOKS, *Chief Alaskan Geologist*, Washington, D. C.  
Mexico. VALENTIN R. GARFAS, *Manager, Foreign Oil Department, Henry L. Doherty & Co.*, New York.

## TUESDAY AFTERNOON

Electric Welding of Large Storage Tanks. HAROLD C. PRICE, *Manager Welding Engineering Co.*, Bartlesville, Okla.  
Canada. GEORGE S. HUME, *Canadian Geological Survey*, Ottawa, Ont.  
Central America. ARTHUR G. REDFIELD, *U. S. Geological Survey*, Washington, D. C.  
Ecuador. JOSEPH H. SINCLAIR, *Mining Geologist*, New York.  
Venezuela. EDWIN B. HOPKINS, *Consulting Geologist*, New York, and CHESTER W. WASHBURN, *Consulting Geologist*, New York.  
Peru. V. F. MARSTERS, *Consulting Geological Engineer*, Kansas City, Mo.  
Colombia. L. G. HUNTLEY, *Consulting Geological Engineer*, Pittsburgh, Pa.  
British Empire. ERIC BRUXTON, *Commercial Secretary, British Embassy*, Washington, D. C.  
France and the French Colonies. P. MARTIGNAN, M. & M. E., *Technical Assistant, Commercial Attaché, French Embassy*, New York, N. Y.  
Persia. SULTAN M. AMERIE, *Commercial Attaché, Persian Embassy*, Washington, D. C.  
India. WILLIAM J. WRIGHT.

Europe and Asia. HENRY C. MORRIS, *Chief, Petroleum Division, Department of Commerce, Washington, D. C.*  
Business Session.

### *Coal and Coke, Ground Movement and Subsidence*

MONDAY MORNING, FEB. 18

Chairman, Howard N. Eavenson

Address of welcome, by Chairman, to Dr. R. V. Wheeler, *Director, British Safety in Mines Station at Eskmeals*, and to H. Eustace Mitton, *Member of Council, Institution of Mining Engineers*.

Reply by Doctor Wheeler, telling of coöperation entered into by British and American Governments in investigations relating to the prevention of mine accidents.

Acknowledgment by Mr. Mitton.

Illustrated talk on Mining Methods Observed in European Countries and Methods of Restoring Coal Mines of Northern France. GEORGE S. RICE, *Chief Mining Engineer, Bureau of Mines, Washington, D. C.*

MONDAY AFTERNOON

Chairman, H. G. Moulton

Report by George S. Rice of the results of his discussions with foreign technical societies, regarding the collection and interchange of data on ground movement and subsidence, followed by his illustrated description of instances of subsidence observed in metal mining and coal mining, and methods taken to prevent damage from subsidence.

### *Coal*

TUESDAY MORNING, FEB. 19

Chairman, Howard N. Eavenson

Coal Mining by the V System. GLENN B. SOUTHWARD, *Chief Engineer, West Virginia Coal & Coke Co., Elkins, W. Va.*

Dry Cleaning of Coal. RAY W. ARMS, *Contracting Engineer, Roberts & Schaefer Co., Chicago, Ill.*

Valuation of Coal Mining Properties in the United States. *Report of Engineers' Advisory Valuation Committee to the U. S. Coal Commission.*

Data Respecting Labor Employed in Various Bituminous Mines. HOWARD N. EAVENSON, *Mining Engineer, Pittsburgh, Pa.*

Discussion of Report of U. S. Coal Commission. E. W. PARKER, *Director, Anthracite Bureau of Information, Philadelphia, Pa.*

### *Committee on Drill Steel*

MONDAY MORNING, FEB. 18

Chairman, D. A. Lyon

Open Session of Advisory Board to Bureau of Mines and Bureau of Standards on Drill Steel Breakage and Heat Treatment.

The Hawkesworth Detachable Bit. R. S. ALLEY, *President, Hawkesworth Drill Co.* Report to the Advisory Board.

Physical Defects in Hollow Drill Steel. FRANCIS B. FOLEY, *Metallurgist, Bureau of Mines, Rolla, Mo.*; CHARLES Y. CLAYTON, *Professor of Metallurgy, Missouri School of Mines and Metallurgy, Rolla, Mo.*; MUIR L. FREY, *Junior Metallurgist, Bureau of Mines, Rolla, Mo.*

Survey of Iron and Steel Equipment Used in Oil Well Drilling.

*Metallurgy*

MONDAY AFTERNOON, FEB. 18

Chairman, Lawrence Addicks

Direct Electrolysis of Black Copper Anodes of High Nickel-lead Content. M. H. MERRISS, *Metallurgical Engineer, Nichols Copper Co., Laurel Hill, L. I.*

Calculating Zinc for Desilverization of Lead Bullion by the Parkes Process. GEORGE G. GRISWOLD, New York, N. Y.

The Reduction and Refining of Tin in the United States. H. H. ALEXANDER, *Superintendent, Perth Amboy Plant, A. S. & R. Co.*; and J. R. STACK, *Superintendent of Tin Operations, Perth Amboy Plant.*

Present Trend in Treatment of Complex Ores. G. L. OLDRIGHT, *Hydrometallurgist, Bureau of Mines, Salt Lake City, Utah.*

TUESDAY AFTERNOON, FEB. 19

Chairman, Arthur L. Walker

Greenawalt Electrolytic Copper Extraction Process. WILLIAM E. GREENAWALT, *Consulting Metallurgist, Denver, Colo.*

Ammonia Leaching of Calumet and Hecla Tailings. C. H. BENEDICT, *Metallurgist, Calumet & Hecla Cons. Copper Co., Lake Linden, Mich.*, and H. C. KENNY, *Superintendent, Leaching Plant, Lake Linden, Mich.*

Hydrometallurgy of Lead. OLIVER C. RALSTON, *Asst. Chief Metallurgist, Bureau of Mines, Berkeley, Calif.*

Electrolytic Zinc from Complex Ores. U. C. TANTON, *Metallurgist, Bunker Hill & Sullivan Mining Co., Kellogg, Ida.*, and L. T. LEYSON, *Kellogg, Ida.*

*Industrial Relations*

MONDAY AFTERNOON, FEB. 18

Chairman, Sidney Rolle

Reports of Chairmen of Sub-Committees on

Safety. B. F. TILLSON.

Employment and Industrial Organization. ARTHUR NOTMAN.

Education. E. A. HOLBROOK.

Physical and Mental Factors in Industry. DR. R. R. SAYERS.

General Discussion on Industrial Relations.

TUESDAY AFTERNOON

*Joint Session with Mining Section of National Safety Council*

Chairman, R. Dawson Hall

Mine Accident Statistics. W. W. ADAMS.

Magnetic Investigation of Hoisting Rope. R. L. SANFORD.

The Bureau of Mines' Work for Safety. H. FOSTER BAIN.

Mental Hygiene in Industry. T. T. READ.

Round Table Discussion of Safety Questions.

WEDNESDAY MORNING

Chairman, Arthur Notman

Some Recent Experiences in Australia. A. J. LANZA.

Industrial Relations. ROBERT E. TALLY.

Industrial Relations—Dual Responsibilities. L. K. SULLOCH.

Address by D. L. STIRLING, *Secretary, Australasian Institute of Mining and Metallurgy.*

## WEDNESDAY AFTERNOON

Chairman, Sidney Rolle

- The Vital Factor in Industrial Relations. G. M. GILLETTE.  
 Industrial Relations in the European Coal Fields. JOHN T. RYAN.  
 Dust and the Health of the Miners. D. HARRINGTON.  
 A Living Wage to the Worker—If He Earns It. W. R. CHEDSEY.

*Iron and Steel*

MONDAY AFTERNOON, FEB. 18

Chairman, John A. Mathews

- Overstrain in Metals. JOSEPH KAYE WOOD, *Engineer, Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.*  
 The Nature of Martensite. EDGAR C. BAIN, *Research Metallurgist, Atlas Steel Corp., Dunkirk, N. Y.*  
 Effect of Zirconium on Hot-rolling Properties of High-sulfur Steels and Occurrence of Zirconium Sulfide. ALEXANDER L. FEILD, *M. S., Research Metallurgist, Electro Metallurgical Co., New York City.*  
 Micrographic Detection of Carbides in Ferrous Alloys. NORMAN B. PILLING, *Metallurgist, Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa.*  
 Use of Sodium Picrate in Revealing Dendritic Segregation in Iron Alloys. V. N. KRIVOBOK and ALBERT SAUVEUR, *S. D., Professor of Metallurgy and Metallography, Harvard University, Cambridge, Mass.*  
 Simulating Natural Light in Metallography. H. S. GEORGE, *Metallurgist, Union Carbide & Carbon Research Laboratories, Long Island City, N. Y.*

## TUESDAY AFTERNOON

*Iron and Steel and Refractories*

Chairman, J. V. W. Reynders

- Absorption of Sulfur from Producer Gas. J. H. NEAD, *Chief Metallurgist, American Rolling Mill Co., Middletown, Ohio.*  
 Economic Significance of Metalloids in Basic Pig Iron in Basic Open-hearth Practice. C. L. KINNEY, JR., *Superintendent of Open Hearth No. 1, Illinois Steel Co., South Chicago, Ill.*  
 Effect on Steel of Variations in Rate of Cooling in Ingot Mold. WILLIAM J. PRIESTLEY, *Metallurgical Engineer, Electro Metallurgical Sales Corp., Pittsburgh, Pa.*  
 Stainless Steel with Particular Reference to the Milder Varieties. J. H. G. MONY-PENNY, *F. Inst. P., Chief of Research Laboratory, Brown Bayleys Steel Works, Ltd., Sheffield, England.*  
 Effect of Coke Combustibility on Stock Descent in the Blast Furnace. P. H. ROYSTON, *Assistant Metallurgist, Bureau of Mines, Minneapolis, Minn., and T. L. JOSEPH, Associate Metallurgist.*  
 The Story of Fireclay Refractories. *Moving pictures.*  
 Requirements of Refractories for the Open Hearth. F. W. DAVIS, *Metallurgist, Bureau of Mines, Lincoln, Neb., and G. A. BOLE, Superintendent Ceramic Station, Bureau of Mines, Columbus, Ohio.*

*Annual Lecture of Institute of Metals Division*

MONDAY AFTERNOON, FEB. 18

Chairman, Pres. E. P. Mathewson

- The Trend in the Science of Metals: By ZAY JEFFRIES, *Director of Research, Aluminum Castings Co., Cleveland, Ohio.*

*Institute of Metals Division*

TUESDAY AFTERNOON

Chairman, William B. Price

Business Session.

Some Low Copper-nickel Silvers. WILLIAM B. PRICE, *Chief Chemist and Metallurgist, Scovill Mfg Co., Waterbury, Conn.*, and C. G. GRANT, *Metallurgist, Scovill Mfg. Co.*

Corrosion of Brass as Affected by Grain Size. ROBERT J. ANDERSON, *Metallurgist, Bureau of Mines, Pittsburgh, Pa.*, and GEORGE M. ENOS, *Instructor in Metallurgy, University of Cincinnati, Cincinnati, Ohio.*

Relation of Heat Treatment to the Microstructure of 60-40 Brass. ROBERT S. WILLIAMS, *Associate Professor of Metallography, Massachusetts Institute of Technology* and VICTOR O. HOMERBERG, *Instructor in Metallography, Massachusetts Institute of Technology, Cambridge, Mass.*

WEDNESDAY AFTERNOON

Chairman, George K. Elliott

Round Table Discussion on Fluxes and Deoxidizers in charge of W. M. CORSE.

*Joint Session of the Institute and the Society of Economic Geologists*

TUESDAY MORNING

Chairman, James F. Kemp

Collection of Elements to be Installed at American Museum of Natural History. GEORGE F. KUNZ, *New York City.*

Petrographic Studies of Limestone Alterations at Bingham. A. N. WINCHELL, *Professor of Geology and Petrology, University of Wisconsin, Madison, Wis.*

Limestone Ores of Bingham, Utah. RICHARD N. HUNT, *Mining Geologist, Los Angeles, Calif.*

Geological Features and Court Decisions of the Bingham District. ORRIN P. PETERSON, *Consulting Geologist, Brookline, Mass.*

Magnetite Deposits of Eastern Porto Rico. CHARLES R. FETTER, *Ph.D., Associate Professor of Geology and Mineralogy, Carnegie Institute of Technology, Pittsburgh, Pa.*

TUESDAY AFTERNOON

*Symposium on Secondary Enrichment*

Chairman, James F. Kemp

The subject was introduced by the CHAIRMAN, after which the following papers were presented:

Organization and Operations of the Secondary Enrichment Investigation. L. C. GRATON.

Rock Alteration Associated with Copper Sulfide Deposits in Igneous and Schistose Rocks. EDWARD H. PERRY, AUGUSTUS LOCKE, and L. C. GRATON.

Oxidation and Enrichment at Ducktown, Tenn. GEOFFREY GILBERT.

Oxidation and Enrichment in Shasta County, Calif. L. C. GRATON.

WEDNESDAY MORNING

Chairman, James F. Kemp

Copper Deposits in the Nikolai Greenstones, Kuskulana-Kotsina District, Alaska. ALFRED WANDER.

The Origins of Rich Silver Ores. EDSON S. BASTIN.

Primary Downward Changes in Ore Deposits. W. H. EMMONS.

Fundamental Conceptions of Secondary Copper Sulfide Enrichment. L. C. GRATON.



## WEDNESDAY AFTERNOON

Habit, Etch Structure and Geological Significance of Chalcocite. ALFRED WANDKE.  
 Role of Secondary Enrichment in Genesis of Butte Chalcocite. AUGUSTUS LOCKE,  
 D. A. HALL and M. N. SHORT.

Primary or Secondary Chalcocite? The Case for Deep Bornite Enrichment. L. C.  
 GRATON, D. H. McLAUGHLIN, M. N. SHORT and ALFRED WANDKE.

General Open Discussion of Secondary Enrichment and Other Vertical Changes in  
 Grade of Ores.

*Mining Methods*

TUESDAY MORNING, FEB. 19

Chairman, B. B. Gottsberger

Development of Mine Transportation in Clifton-Morenci District, Arizona. NOR-  
 MAN CARMICHAEL, formerly General Manager, The Arizona Copper Co., and JOHN  
 KIDDIE, Mine Superintendent, Phelps Dodge Morenci Branch, Morenci, Ariz.  
 Mining Methods of Telluride District. CHARLES N. BELL, Mining Engineer, Denver,  
 Colo.

Fresnillo Glory-hole Mining Practice. THOMAS C. BAKER, Assistant to General  
 Manager, The Mexican Corp., Fresnillo, Mexico.

Business Session.

## WEDNESDAY MORNING

Chairman, R. M. Raymond

Alaska-Juneau Mine. P. R. BRADLEY, General Superintendent, Alaska-Juneau Gold  
 Mining Co., Juneau, Alaska.

Mining Methods in Mogollon District of New Mexico. S. J. KIDDER, General Mana-  
 ger, Mogollon Mines Co., Mogollon, N. M.

Geology and Mining Methods in Beatson Mine, Alaska. STEPHEN BIRCH, New York,  
 N. Y.

Geology and Mining Methods in Kennecott Mines, Alaska. STEPHEN BIRCH,  
 New York, N. Y.

Mining Methods and Costs at the Iron Cap Copper Co., Arizona. CHARLES E. LEES,  
 Mine Superintendent, Iron Cap Copper Co., Copper Hill, Ariz.

Sampling and Estimation of Cordilleran Silver-lead Limestone Replacement Deposits.  
 BASIL PRESCOTT, Consulting Geologist, El Paso, Texas.

*Timber Requirements and Reforestation*

TUESDAY AFTERNOON, FEB. 19

Chairman, Charles H. MacDowell

Round Table Discussion

*Contributors*

CHARLES A. MITKE

ALLAN FRENCH

HORACE MOSES

W. D. BRENNAN

ROBERT S. LEWIS

ROBERT GARDINER

E. L. YOUNG

FRED JONES

E. L. HARTWELL

GEORGE O. ARGALL

WILLIAM W. ELMER

JAMES F. MCCARTHY

STANLY A. EASTON

L. K. ARMSTRONG

J. L. BRUCE

W. P. CHINN

J. A. MITCHELL

M. M. DUNCAN

O. A. WILSON

F. C. WALLOWER

M. H. SELLERS

HARRY VIVIAN

R. M. HENDERSON

*Milling*

WEDNESDAY MORNING, FEB. 20

Chairman, Galen H. Clevenger

Paths of Balls in Tube Mills and Rock Crushing by Rolls. Slow Motion Pictures.

H. E. T. HAULTAIN, *Professor of Mining Engineering University of Toronto, Toronto, Ontario*, and F. C. DYER, *Assistant Professor*.Efficiency of Screening. ROBERT K. WARNER, *Assistant Professor of Mining, Yale University, New Haven, Conn.*Surface Reactions in Flotation. A. W. FAHRENWALD, *E. M., Met. E., Ore Dressing Engineer, Bureau of Mines, Moscow, Idaho*.

Discussion of Work of Milling Methods Committee.

*Joint Meeting with the Mining and Metallurgical Society of America*

WEDNESDAY AFTERNOON, FEB. 20

*Opportunities for Mining Engineers*

Chairman, B. B. Gottsberger

New Fields for Mining Engineers in Foreign Countries with Special Reference to the Near East. JOHN WELLINGTON FINCH.

The Engineer's Relation to Bankers. LUCIUS W. MAYER.

Opportunities for Mining Engineers in Coal Mining. R. DAWSON HALL, *Editor Coal Age, New York City*.Opportunities for Mining Engineers in the Rock Products Industry. NATHAN C. ROCKWOOD, *Editor Rock Products*.*Oxygenated Air*

WEDNESDAY AFTERNOON, FEB. 20

Chairman, Bradley Stoughton

Use of Oxygen or Oxygenated Air in Metallurgical and Allied Processes. F. W. DAVIS, *Metallurgist, Bureau of Mines, Washington, D. C.*Enriched Air in Metallurgy. W. S. LANDIS, *Vice-president, American Cyanamid Company, New York, N. Y.*Effect of Oxygen-enriched Air in Roasting of Zinc Ores. B. M. O'HARRA, *Associate Metallurgist, Bureau of Mines, Rolla, Mo.*; WILLIAM KAHLBAUM, *Research Chemist and Metallurgist, Missouri School of Mines and Metallurgy, Rolla, Mo.*; E. S. WHEELER, *Assistant Research Metallurgist, Missouri School of Mines and Metallurgy*; and W. J. DARBY, *formerly Graduate Fellow in Metallurgy, Missouri School of Mines and Metallurgy*.

Cheap Oxygen in Metallurgy. EDMUND B. KIRBY.

Discussion was conducted under the following subheads

Use of Oxygenated Air in Iron Blast Furnace.

Use of Oxygenated Air in Ferro-alloys.

Use of Oxygenated Air in General Non-ferrous Metallurgy.

Application of Oxygen to Bessemerizing.

Use of Oxygenated Air in Gas Producers.

Economical Production of Oxygen.

*Contributors*A. N. DIEHL  
LEDYARD HECKSCHER  
R. H. SWEETSER  
LEO D. JONESH. A. WHEATON  
WALDEMAR DYRSSEN  
R. B. MOORE  
CHARLES HART

## PRESENTATION OF JAMES DOUGLAS MEDAL

The gold medal established in honor of Dr. James Douglas, awarded for the first time in 1923 to Frederick Laist, was presented to Charles Washington Merrill for his achievements in metallurgy, his inventions, and especially his improvements in cyanide practice.

## SOCIAL EVENTS

The annual banquet at the Waldorf was one of the largest the Institute has held and was a great success.

The Woman's Auxiliary, as usual, arranged entertainment for the visiting ladies throughout the meeting.

# PAPERS



## What is Steel?<sup>\*</sup>

BY ALBERT SAUVEUR,† CAMBRIDGE, MASS.

AS THE years go by, names of distinguished metallurgists will be added to the list of Henry Marion Howe lecturers, and now and then an illustrious one, for to be chosen to deliver the Howe lecture will be, I do not hesitate to predict, a highly coveted honor. I pray, therefore, your indulgence, if I confess to a feeling of gratification in having been appointed the first of these lecturers. It does not follow, however, that I am losing all sense of proportion and that I have an exaggerated idea of the little I have been able to contribute to our knowledge of iron and steel. Indeed, I fully realize how small were my claims to so great a distinction. I realize, also, that those entrusted with the task of selecting a lecturer were actuated, in coming to a decision, by their knowledge of the long and intimate friendship that had existed between the leader we have lost and myself. For their generous impulse, I thank them from the bottom of my heart; and with becoming modesty, I take up my task as the first Henry Marion Howe lecturer.

It would be pleasant and indeed most appropriate to devote this entire lecture to a eulogy of Henry Marion Howe and his work, but how short the time for so large an undertaking and how inadequate my qualifications.

On Aug. 28, Sept. 4, 11, and 18, 1875, a series of articles appeared in the *Engineering & Mining Journal* entitled "What is Steel?" With one exception, these constitute the first professional paper of Henry Marion Howe. That was nearly fifty years ago, three years after graduating from Harvard University. He was then but twenty-seven years old and already his keenly inquisitive mind was actively at work. There is a touch of romance in this young metallurgist who, on entering his scientific career, destined to be so brilliant and so fruitful, on the very threshold of it, seems to have selected as his motto "What is Steel?" Like a knight-errant of science, he started on his quest for an answer to that question, a quest which was to last forty-seven years and which death only brought to an end. And while thus engaged how many wonderful messages we received from him, each one bringing us nearer to the goal! How illuminating, inspiring and encouraging were those messages! How well equipped he was to wrench from nature some of the secrets she so jealously guards! How broad his learning and how clear his

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<sup>\*</sup>First Annual Henry Marion Howe Memorial Lecture, delivered at the New York Meeting of the American Institute of Mining and Metallurgical Engineers, Feb. 19, 1924.

† Professor of Metallurgy and Metallography, Harvard University.

vision! How great his courage and his genius for work! How kind and generous his nature! How passionate his love of humanity and democracy and his abhorrence of injustice and tyranny! How many of us on the point of going astray were called back to the right path by Howe's guiding torch! How much we owe him and how much we love him!

That Howe should have been able to impart to others the totality of his knowledge may be doubted, while unfortunately it has not been possible for him to communicate to others the faculty he had of using that knowledge through his extraordinary power of coördination. This is an irreparable loss. The bricks he has left us, but where is to be found the mason capable of adding with equal speed and skill to the harmonious structure that Howe was building, a structure to which many of us will make modest contributions but which of necessity, according to the dictates of nature, must forever remain incomplete. If nature, however, is so reluctant to have her secrets divulged, she should not permit the birth of men equipped for wrenching those secrets from her. In doing so, she follows the course of the maker of war materials who, as soon as he has covered his ship with armor plates believed to be invulnerable, bends his efforts to the construction of a projectile capable of piercing them. To be sure, but few of these human projectiles are born, and it is only in spots that nature's protective armor has been pierced.

In selecting for my lecture the same title as the one given by Howe to his early articles, I do not intend to convey the impression that I have the answer to that question; I merely desire to indicate that we are still following his footsteps.

Howe's professional papers can be counted but their value cannot be estimated. They cover the entire field of the metallurgy of iron and steel and the study of the nature and properties of these important metals.

In 1875, when young Howe entered the metallurgical field, our conception of the nature of steel was very crude and our treatment of it purely empirical, while its manufacture in the United States was still in its infancy. Bessemer steel was first made in 1864, and three years later, in 1867, we produced only 2679 tons of it. Open-hearth steel was first made in 1868, and in 1869 we manufactured only 900 tons. During his long career, Howe witnessed the growth of the steel industry from these insignificant productions to yearly tonnages reaching nearly 40,000,000 tons of pig iron, 12,000,000 tons of bessemer steel, and 35,000,000 tons of open-hearth steel. The treatment of steel was developed into an accurate science, while our knowledge of the true constitution, behavior, and properties of that metal made wonderful progress. To these developments, Howe contributed more than any single metallurgist—indeed, possibly more than any two or three of them.

As early as 1876, he discussed the thermic curves of blast furnaces. In 1882, he suggested a cure for blast-furnace chills; in 1908, he made a critical study of the shape of the iron blast furnace; while in his book, "Iron, Steel and Other Alloys," published in 1906, he devotes an important chapter to the reactions of the blast furnace and to its operation.

He discusses the bessemer process in several of his professional papers, giving special attention to the attainment of uniformity. It is hardly necessary to recall his masterly description of bessemer plants and their equipment in his "Metallurgy of Iron and Steel," published in 1890. In 1899, he discussed the Bertrand-Thiel open-hearth process; in 1908, the duplex process for steel making; and, in 1902, the progress in the open-hearth process since 1899. In 1922, Howe and Barba published several papers dealing with the acid open-hearth process for the manufacture of gun steels and fine steels.

His study of the crucible-steel process in his "Metallurgy of Steel" will long remain a classic. In 1909, he gave his attention to the treatment of steel in electric furnaces. To the production of sound and homogeneous steel ingots and other castings, Howe gave much thought. Not less than sixteen of his papers, published between 1907 and 1915, deal with that important subject. He discussed with rare lucidity the prevention of piping, the closing and welding of pipes and blowholes, the influence of ingot size on segregation, etc. In his "Metallurgy of Steel" these subjects are exhaustively treated.

The corrosion of iron and steel received from him the attention which the importance of the subject demands. In three of his papers, he discusses "The Relative Corrosion of Wrought Iron and Steel."

Alloy or special steels were quite unknown in 1875. Howe, therefore, witnessed the birth of these important alloys and their growth to their present important position. To this development he contributed abundantly. What might be called the alloy-steel era was practically ushered in by Sir Robert Hadfield's discovery of manganese steel in 1882. Howe devoted much time to the study of that remarkable metal. Four of his professional papers deal with it, while he patented a manganese-steel mold and a process of making manganese steel.

To a logical nomenclature of iron and steel, he devoted much study. His first paper "What is Steel?" already mentioned, was followed by many others dealing with that subject in 1876, 1906, 1909, and 1912. He also proposed a nomenclature of the microscopic constituents of iron and steel, which has been universally adopted.

Endowed with the rare gift of clear thinking, and hence of clear exposition, his teaching was a source of inspiration to his students. He wrote a number of important papers dealing with the art of teaching metallurgy and with the equipment of metallurgical laboratories. In 1902, he published his well-known laboratory book entitled "Metallurgical Laboratory Notes."



Doctor Burgess writes that Professor Howe's courses at Columbia University were considered the easiest in the school. No greater compliment could be paid to a teacher. It testifies not to the simplicity of his subject but to his mastery of it.

While Howe studied every phase of the manufacture of iron and steel and contributed to its advancement, because of the quality of his mind, he was naturally attracted with greater force by the scientific aspect of metallurgy. The profound study he made of the constitution of iron-carbon alloys, of their microstructure and thermal treatment, of what is sometimes called the physics of steel, and his brilliant discussions of these subjects will forever remain deeply engraved in our minds. As he proceeded in his journey, he left behind him many landmarks which make it possible for us to follow his trail in an attempt to reap a little of what he sowed. His first paper on the heat treatment of steel was published in 1888, while in 1891, in his monumental work "The Metallurgy of Steel" his description of the crystallization, heat treatment, and physics of steel marked an epoch in our scientific study of that metal. This was followed, in 1916, by the publication of his "Metallography of Steel and Cast Iron" where his genius carried him far ahead of his time. It was the publication of that book which led me to refer to him on the occasion of the presentation of the John Fritz Medal "as a voyager in realms but dimly perceived by his fellow-workers, as a lone explorer of fields destined to yield rich harvests to future generations."

Howe teaches us to beware of hasty conclusions. The claims so frequently and lightly made by some writers that they have proved their contentions are seldom found in Howe's writings. He is not carried away by new theories to the extent of discarding all others. He gives to each the weight to which it is entitled and draws guarded and sound conclusions. It is excusable on the part of exponents of new theories that they should be unintentionally biased. They, of necessity, wear glasses through which they perceive a universe in complete harmony with their conceptions. For some, it is an amorphous universe; for others, it is colloidal; while others still can see it only through space lattices. Again, some claim it to be governed solely by the phase rule. Outsiders, however, should not wear the same glasses; they should be receptive but not too credulous. We should examine new theories as a workman examines new tools and use them with discrimination, avoiding too hasty a discard of older tools. There was a time when no paper on metallography could be written without prefacing it by a description of the phase rule. No metallurgical phenomenon was to be explained without its help. When I published my "Metallography," in 1912, I was criticized by some for not having devoted my first chapter to the phase rule, instead of leaving it for the last chapter. Such criticisms are not made today, the phase rule having been given the place it should log-

ically occupy in our metallurgical studies. And so it will be with colloidal theories,  $x$ -ray analysis, and other modes of investigation, mental or physical, devised by man's ingenuity. When we are told that the fuzzy lines of the  $x$ -ray spectrum prove the existence of ultramicroscopic crystals of alpha iron, and that the existence of these small crystals is the obvious reason why quenched steel is hard, we should listen attentively, but we should not too lightly accept the claim that the problem of the hardening of steel has been taken out of the realm of speculation by this new method of investigation.

When acrobatics performed by atoms are described to us and offered with considerable insistence on its finality as an explanation of the phenomena of diffusion, solid solution, etc., it is well to remember that imagination also plays an important part in this explanation.

By now describing briefly the results of some experiments conducted in the Metallurgical Laboratory of Harvard University, I trust I am not wrong in assuming that, should I succeed in adding a little to our knowledge of the metals in which Howe was so deeply interested, I shall in a way honor his memory. May it not be compared to the kind of tribute intended by an author in dedicating his work to one for whom he entertains feelings of respect, admiration, and affection? These experiments seem to establish the fact that thermal ranges of critical plasticity exist in some iron-carbon alloys. It does not appear that the existence of such ranges had been observed before, or at least not as clearly as we have been able to observe them. This investigation forms part of the thesis presented by Dai Chin Lee for the degree of Doctor of Science. They were conducted by Doctor Lee with great skill and thoroughness. For lack of time, I am able only to give a brief outline of this investigation and to call attention to the most significant results.

#### ARMCO INGOT IRON

Bars of Armco ingot iron were twisted at different temperatures using the arrangement shown in Fig. 1. The bar  $S$  to be tested is placed in an electrically heated tube furnace from which it protrudes at both ends. One end is firmly held in a vise  $V$  while to the other end, supported by passing through a hole in a plate  $U$ , is attached the wheel and crank  $H$  by which the bar is twisted. The temperature of the middle of the bar is recorded by the couple  $T$  and potentiometer  $P$ . From its maximum at the middle, the temperature of the bar decreases gradually in both directions, resulting in equal temperatures prevailing at equal distances to the right and left of the center. The bars tested were  $\frac{1}{4}$  in. square, and twisting was applied at a uniform speed when the following temperatures, in degrees centigrade, were obtained at the middle of the bars: 600, 750, 830, 900, 910, 915, 930, 940, 980, 1000, 1020, 1050,

1100, 1200. A bar was also twisted at room temperature. In every instance the twisting was continued until fracture occurred.

The results obtained are clearly shown in Fig. 2*a*. It will be noted that as long as the temperature of the middle of the bar did not exceed 900° C., the twisting and final fracture took place in the middle. The beginning of the  $A_{c_3}$  point in this iron was found to be at 910° C. Below 910° C., it is therefore alpha iron that we are twisting and fracture

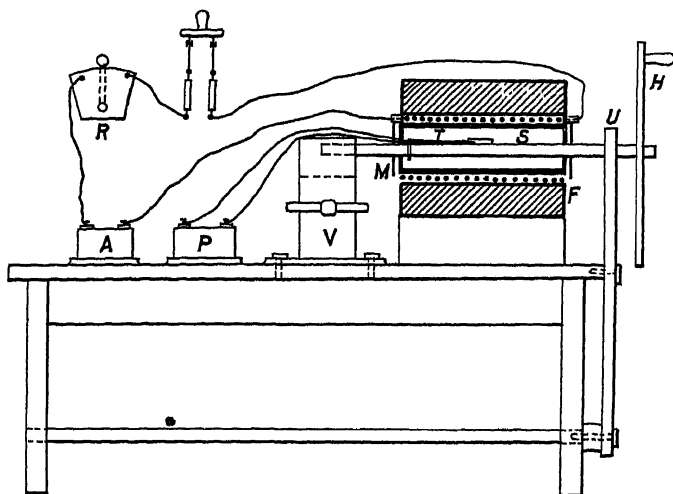


FIG. 1.—HEATING ARRANGEMENT FOR TWISTING TESTS.

takes place at or near the middle of the bar; that is, where alpha iron has been heated to the highest temperature. It follows that the malleability of alpha iron increases with the temperature, being maximum at the highest temperature at which alpha iron can exist, namely, at about 900°. This result was to be expected. As soon as the temperature of 910° C. is exceeded, however, the middle of the bar is in the gamma condition, while at some distance in both directions the iron is in the alpha state. Now twisting occurs not at the center of the bar, where the temperature is highest, but at two places equidistant from the center and necessarily at equal temperatures and rupture finally takes place at one of these places. We naturally infer that these portions of ready twisting must be near or at 900° C. Here two inferences are permitted: (1) alpha iron at the highest temperature at which it can exist, namely, in the vicinity of 900° C., is more plastic than gamma iron at 940°, 980°, 1000°, and even at 1020° C.; or (2) when iron undergoes its alpha-gamma transformation, it acquires a temporary plasticity that greatly exceeds the plasticity of gamma iron at considerably higher temperatures. In view of the very local character of the twisting and of other evidences, which lack

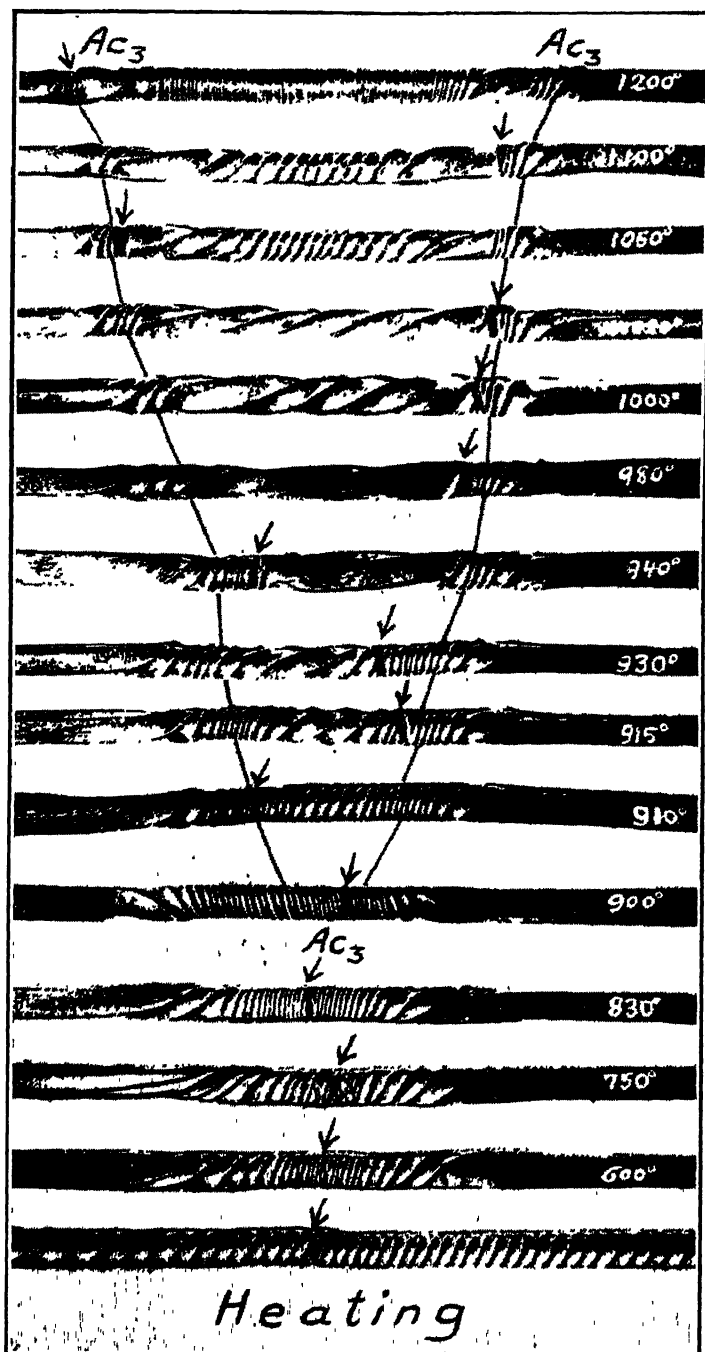


FIG. 2a — ARMCO INGOT IRON

of time does not permit me to describe, the second conclusion seems more likely to be the correct one. As the temperature of the center of the bar increases, the critically twisted portions are located at increasing distances from that center. It will be noted that the plasticity of the gamma

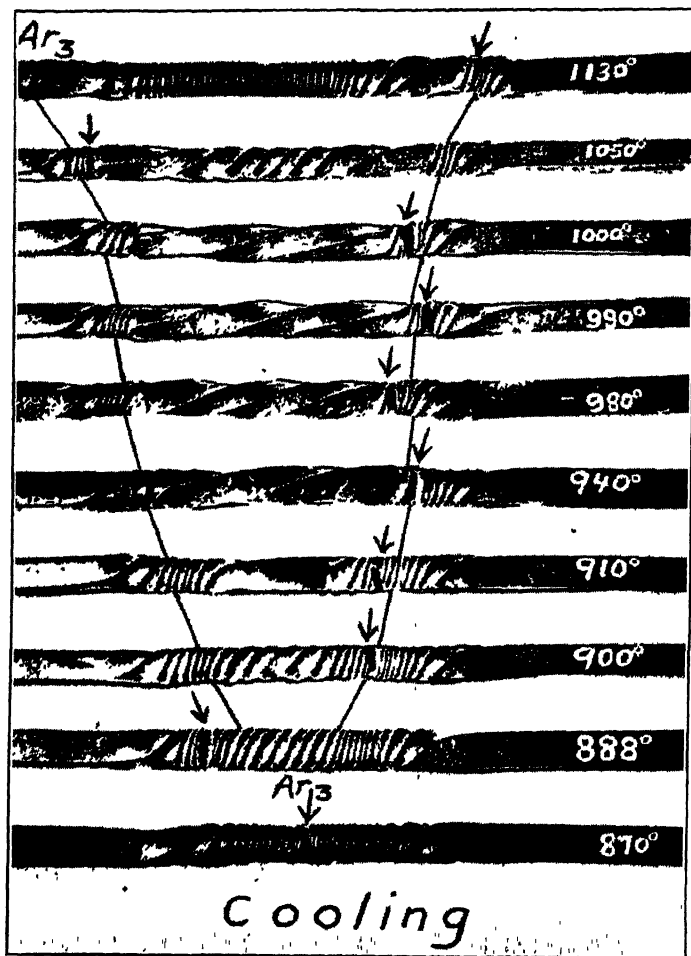


FIG. 2b.—ARMCO INGOT IRON.

portion increases until it actually becomes greater than the plasticity of the portion undergoing allotropic transformation, but this condition is not reached before the temperature exceeds 1020° C. At 1200° C., the plasticity of gamma iron is very pronounced. The mechanism of this preferential twisting may be described as follows, assuming the bar to have been heated at the center to 1000° C.: twisting occurs locally at two

places equidistant from the center, where the iron is undergoing allotropic transformation and where the temperature, therefore, is in the vicinity of  $900^{\circ}\text{C}$ . This twisting strengthens the twisted iron, which now resists further twisting, causing the gamma portion to twist. This twisted gamma iron being strengthened in turn and resisting further twisting, final twisting and fracture generally occur at one of the two critically twisted portions. As the temperature increases, the twisting of the gamma iron becomes more pronounced. The great resistance to twisting of gamma iron between  $940^{\circ}$  and  $980^{\circ}\text{C}$ . should be noted. The results of these experiments justify, I believe, the placing of the range of relative non-malleability or of red shortness in Armco ingot iron at between  $900^{\circ}$  and  $1025^{\circ}\text{C}$ ., and the statement that this lack of plasticity is maximum between  $930^{\circ}$  and  $1000^{\circ}\text{C}$ .

These tests were repeated on falling temperature, Fig. 2b, that is, when portions of the bars equidistant from the middle were undergoing the  $Ar_3$  transformation. This was obtained by heating the bars until the temperature at the middle exceeded, by  $50^{\circ}\text{C}$ ., the desired temperature; the current was then shut off, and twisting applied as soon as the temperature desired was recorded. The point  $Ar_3$  had been located in the usual manner at  $890^{\circ}\text{C}$ . The results obtained agree with those resulting from twisting on a rising temperature. The critically twisted portions of the bars correspond closely to the  $Ar_3$  transformation.

#### ELECTROLYTIC IRON

Similar twisting tests were applied to bars of electrolytic iron of great purity. The results are shown in Fig. 3. The  $Ac_3$  transformation in this iron was found to begin at  $915^{\circ}\text{C}$ . The bar tested while the middle had reached  $890^{\circ}\text{C}$ ., that is, while it was still in the alpha condition, twisted readily in the center. At  $920^{\circ}\text{C}$ ., critical twists are to be observed very probably at those portions that were undergoing the alpha-gamma allotropic transformation and these critical twists become more distinct and occur at increasing distances from the center as the temperature increases. They still persist in the bar heated in the middle to  $1080^{\circ}\text{C}$ .; iron undergoing its allotropic transformation in the vicinity of  $900^{\circ}\text{C}$ . is more plastic than gamma iron at  $1000^{\circ}\text{C}$ . At  $1200^{\circ}\text{C}$ ., however, the plasticity of gamma iron is so great that it exceeds that of iron undergoing its allotropic transformation, resulting in the disappearance of critical twists.

We naturally infer from these results that electrolytic iron, like Armco iron, possesses a temperature range of relative non-malleability extending from some  $900^{\circ}$  to  $1000^{\circ}\text{C}$ .

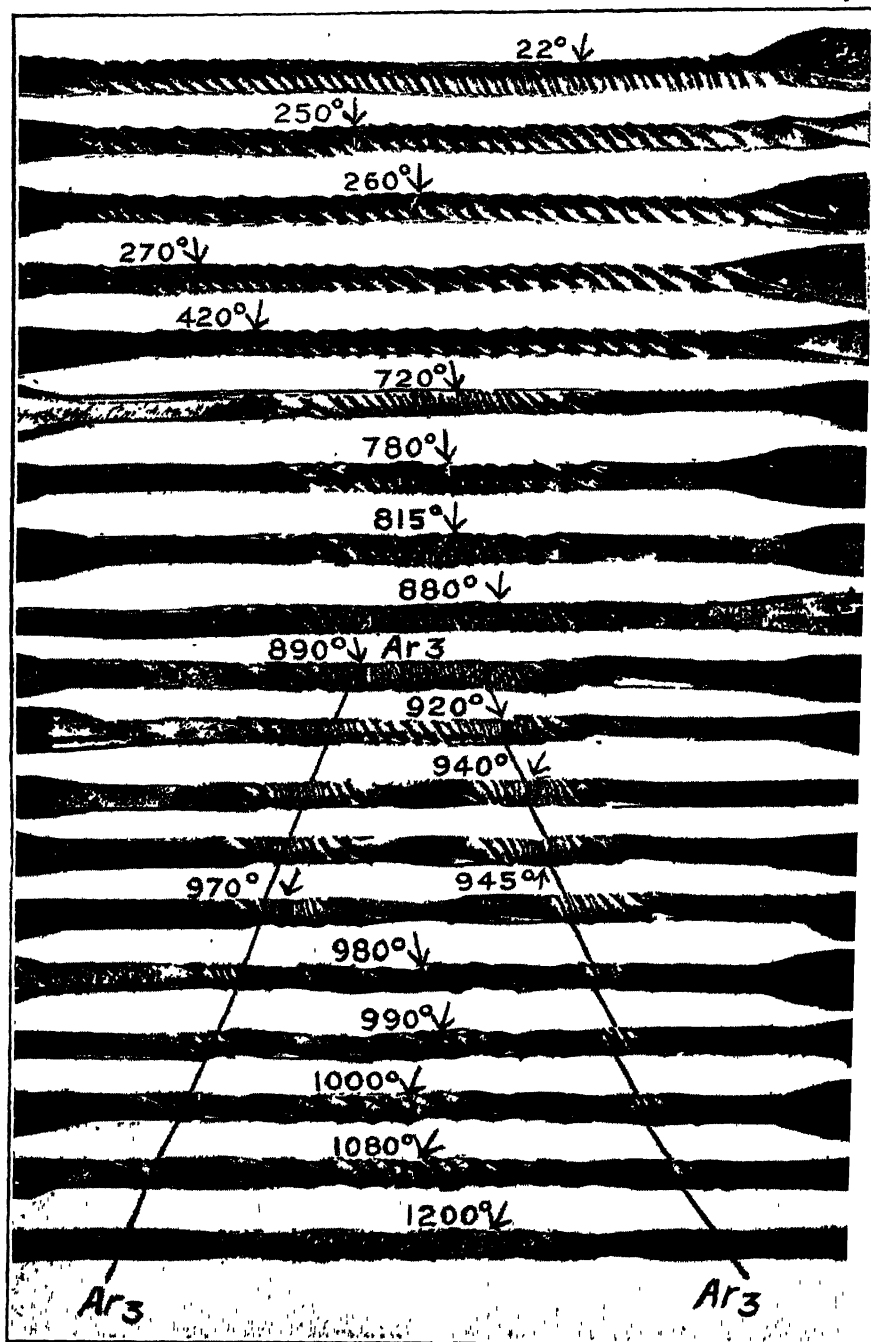


FIG. 3.—ELECTROLYTIC IRON.

## NORWAY IRON

A Norway iron bar, Fig. 4, twisted when the center was heated to 1020° C. clearly shows critical twists indicative of greater plasticity at about 900° C.

## LOW-CARBON STEEL

Bars of commercial steel containing 0.10 per cent. carbon, after being subjected to these differential heatings followed by twisting, yielded the results shown in Fig. 5. The tests were performed on falling temperatures. In this steel the  $A_{r_3}$  point was located at 853° C. The bars heated, at the center, to temperatures inferior to 850° C., and tested therefore while the ferrite was in the alpha condition, twisted and

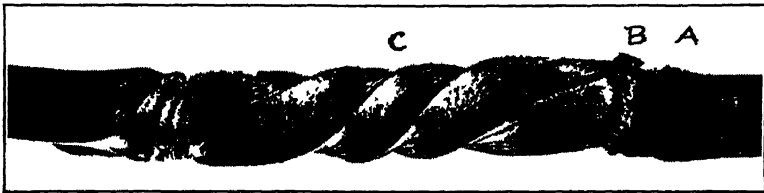


FIG. 4.—NORWAY IRON AT 1020° C.

fractured in the center. Heating to 875° C. and to 900° C., however, results in the occurrence of critical twists, corresponding probably to the portions of the bars that were undergoing their transformation,  $A_{r_3}$ , and again revealing the fact that iron is then more plastic than gamma iron at a considerably higher temperature. At 975° C. and higher temperatures, the bars are more plastic in the center and critical twists no longer occur. We may conclude that steel containing 0.10 per cent. carbon has a thermal range of relative non-malleability, if not of red shortness, extending from some 850 to 975° C.; it seems to be most pronounced at about 900° C.

Having uncovered a range of reduced malleability in steel containing 0.10 per cent. carbon apparently as wide as that which had long been known to exist in Armco iron, it will naturally be asked why the rolling and forging of low-carbon steel is not attended with the same difficulty. A tentative explanation may be offered. It is in the region of reduced malleability that the absence of sulfur is more likely to cause red shortness, unless counteracted by sufficient manganese. In Armco ingot iron, there is very little sulfur, to be sure, but there is also very little manganese. Even this extremely small percentage of sulfur, in the nearly complete absence of manganese, may result in red shortness in the zone of reduced malleability. Well-made low-carbon steel, although much



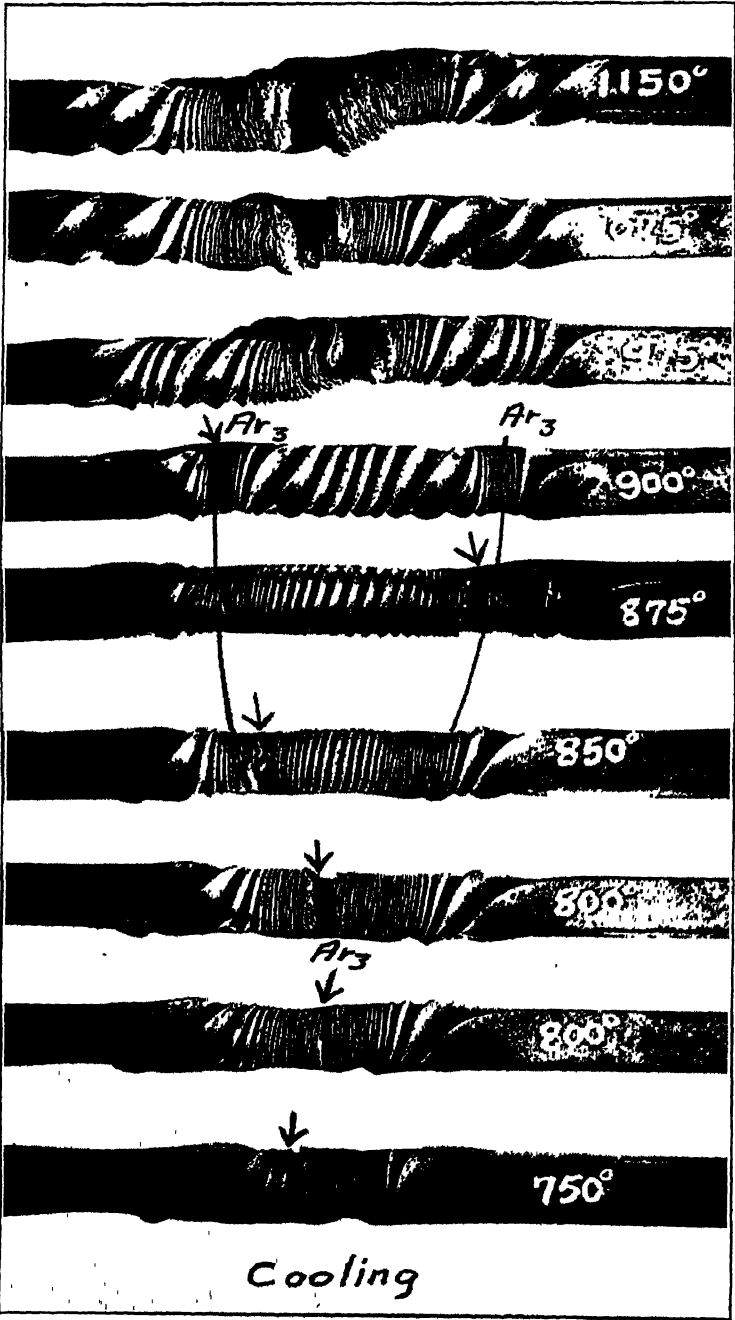


FIG. 5.—0.10-PER CENT. CARBON STEEL.

higher in sulfur than Armco iron, always contains sufficient manganese to prevent red shortness in what might be called the critical working range. The following observations add much weight to the strength of this reasoning: When the sulfur content in Armco ingot iron is less than 0.01 per cent., the metal can be rolled through the critical working range without any indication of red shortness in the practical absence of manganese, while if the sulfur is about 0.03 per cent., it will likewise be possible to work through that range, provided the percentage of manganese is above 0.12 per cent. Impossibility of rolling while the metal is cooling through its range of reduced malleability without inducing red shortness results from the presence of sulfur not completely neutralized by manganese, and in the nearly complete absence of manganese, as in Armco ingot iron, a very small amount of sulfur will suffice. Hence the ease with which we can roll low-carbon steel while it cools through its range of reduced malleability and the difficulty attached to the same operation performed with Armco iron of usual composition.

#### STEEL CONTAINING 0.30 PER CENT. CARBON

Differential heating and twisting of commercial steel containing 0.30 per cent. carbon, performed on rising temperatures, gave the results shown in Fig. 6. This steel exhibited the  $A_{c_3}$  point at  $750^{\circ}\text{C}$ . and the  $A_{c_1}$  point at  $708^{\circ}\text{C}$ . Heating the bars in the center to  $750^{\circ}\text{C}$ . and lower temperatures followed by twisting resulted in causing them to twist in the center where alpha iron was hottest and therefore most plastic. At  $775^{\circ}\text{C}$ . the  $A_{c_3}$  point was exceeded and the center of the bar was in the gamma condition; critical twists now appear in those portions that were undergoing transformation. At  $800^{\circ}\text{C}$ . and higher temperatures, the critical twists disappear, the gamma solid solution or austenite existing at the center being now more plastic. Steel containing 0.30 per cent. carbon appears to possess a narrow range of relative non-malleability (or of reduced malleability), extending from  $770$  to  $800^{\circ}\text{C}$ .

In steel containing 0.50 per cent. or more carbon, the critical twists or critical contractions just described do not occur, Fig. 7. This must be ascribed to the austenite existing above the  $A_{s,2}$  or  $A_{s,2,1}$  points in these steels having greater plasticity than the same steels during their allotropic transformations. Note how greatly reduced is this range in steel containing 0.30 per cent. carbon; we naturally infer that carbon increases the plasticity of gamma iron. It should also be observed that the critical twists seem to be closely related to the  $A_3$  point, as they disappear when the  $A_3$  point merges with the  $A_2$  point, that is, in steel containing some 0.40 per cent. or more carbon.

The thermal range of reduced malleability in iron-carbon alloys to which attention has been called may be provisionally and approximately represented as in Fig. 8, where it covers the area  $ABC$ .

## STAINLESS STEEL

Applying similar tests to stainless steel containing 11.90 per cent. chromium, and 0.32 per cent. carbon, it will be seen that at 750° C. the bar twists and ruptures readily in the center, Fig. 9. Heated to 900° C.

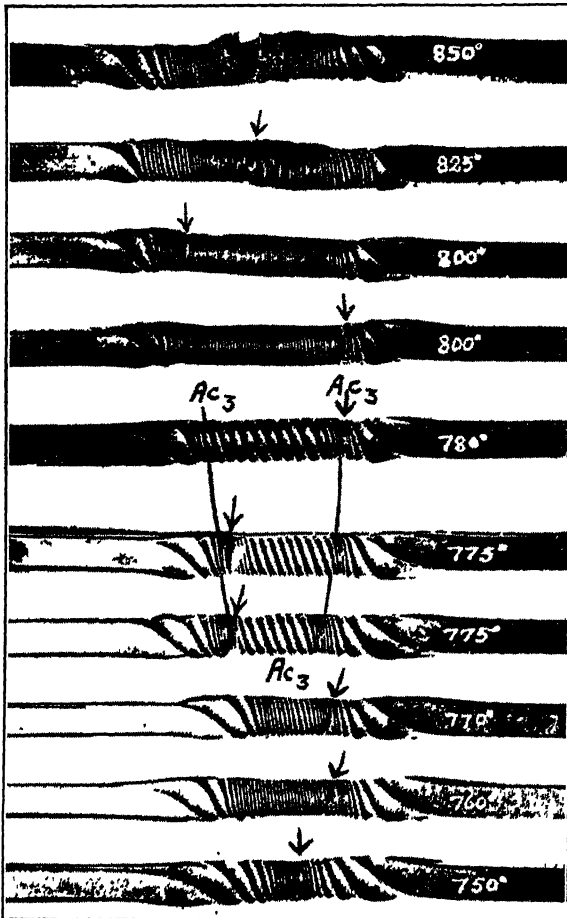


FIG. 6.—0.30-PER CENT. CARBON STEEL.

at the center, marked critical twists occur, the hottest part of the bar being very resistant to twisting. This steel exhibited an upper critical point on heating at 871° C. A thermal range of marked reduced malleability appears to exist in steel of this composition.

The existence of regions of critical plasticity in bars of iron and steel differentially heated may also be revealed by tensile tests, the bars

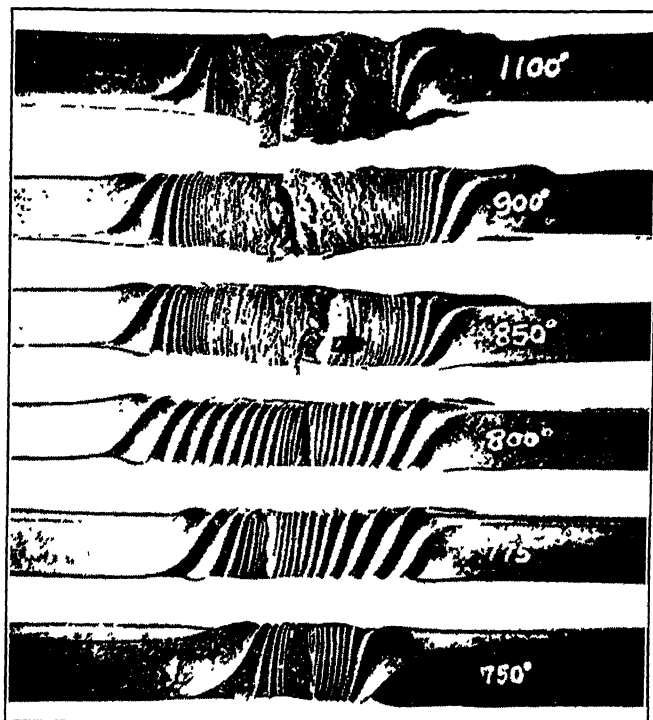


FIG. 7.—0.50-PER CENT. CARBON STEEL.

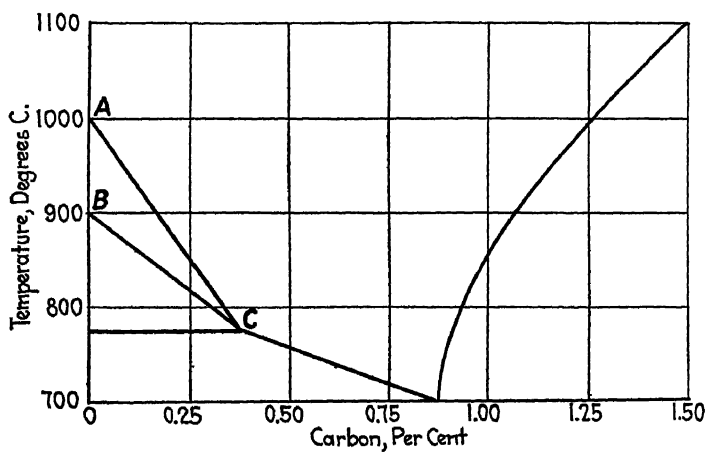


FIG. 8

being placed in a short tube electrically heated while being tested, Fig. 10. It will suffice to present the results obtained with steel containing 0.10 per cent. carbon, Fig. 11, and with Norway iron, Fig. 12. Critical reductions of areas are obtained corresponding to the critical twists of the torsional tests, the bars finally rupturing at one of the critically reduced sections. It will be noted that so long as the temperature at the center of the bar does not exceed  $850^{\circ}\text{C.}$  for the steel and  $900^{\circ}\text{C.}$  for the iron, the bars contract and rupture at or near the middle,

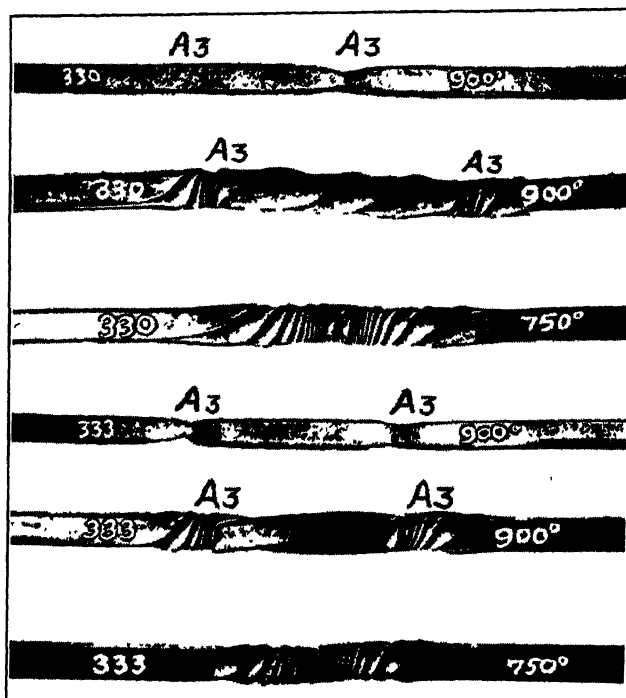


FIG. 9.—STAINLESS STEEL.

that is, where the alpha iron is at the highest temperature. On increasing the temperature at the center of the bars, critical reductions occur equidistant from the center, in all probability in the portions of the bars undergoing the  $A_3$  transformation, their plasticity being greater than that of the gamma iron nearer the center, although the temperature of the latter is considerably higher. Critically reduced sections are still observed when the steel bar is heated at the center to  $945^{\circ}\text{C.}$  Higher temperatures were not used for the tensile tests.

The tensile testing of bars of stainless steel, heated at the center to  $900^{\circ}\text{C.}$ , resulted in sharp critical reductions equidistant from that center

and in final rupture at one of these; see Fig. 9. Testing a bar of the same steel, heated in the middle to  $1000^{\circ}\text{C}.$ , caused it to reduce and to fracture at the center. These examples of critical reductions of the portions of the bars undergoing allotropic transformation could be multiplied.

Fig. 13 shows the relations between the temperature at the middle of the test bars and their corresponding tensile strength, elongation and reduction of area, in the case of steel containing 0.10 per cent. carbon; the thermal curve of the steel has also been included. It will be observed

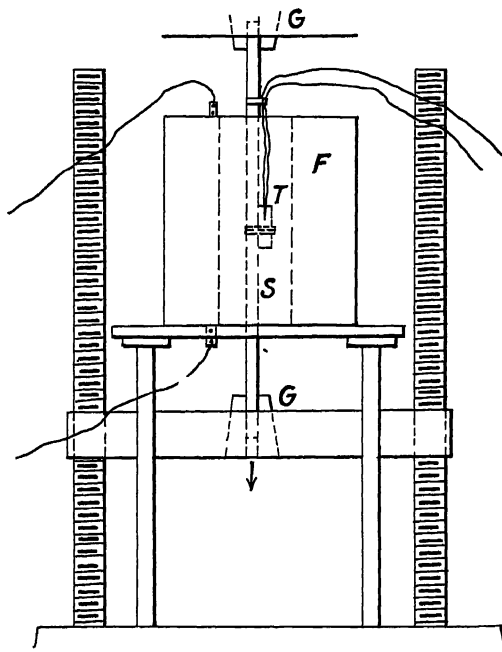


FIG. 10.—HEATING ARRANGEMENT FOR TENSILE TESTS.

that as the temperature increases from  $700^{\circ}$  to  $850^{\circ}\text{C}.$ , the tensile strength decreases quite gradually although there is a change of direction in the curve corresponding to the  $Ar_2$  point. As long as the temperature remains under  $850^{\circ}\text{C}.$ , the fracture of the bars occurs in the center where the temperature was maximum. This portion of the curve discloses the fall of the tensile strength of the aggregate of pearlite and alpha ferrite as the temperature increases. When a temperature of  $850^{\circ}\text{C}.$  is reached which corresponds to the  $Ar_3$  transformation, minimum tensile strength is recorded. On further increase of temperature, the tensile strength at first increases and then remains practically constant between  $875^{\circ}$  and  $950^{\circ}\text{C}.$  This constancy of tenacity results from the fact that all the bars are now breaking at the same temperature, namely  $850^{\circ}\text{C}.$ ,

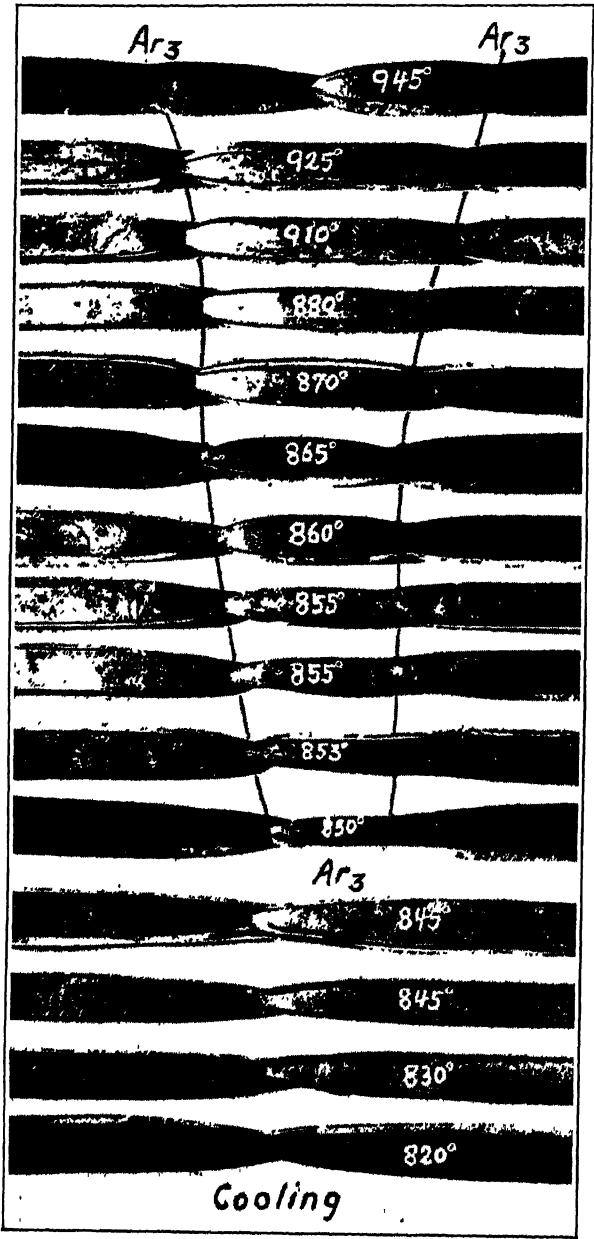


FIG. 11.—0.10-PER CENT. CARBON STEEL.

prevailing at a certain distance from the center. It represents the tensile strength of the steel when undergoing its  $A_{r3}$  transformation. The fact that the bar heated exactly to  $850^{\circ}$  C. at its center broke under a lower stress may possibly be explained on the ground that a longer portion of the bar is then at  $850^{\circ}$  C. than when the center is heated to a

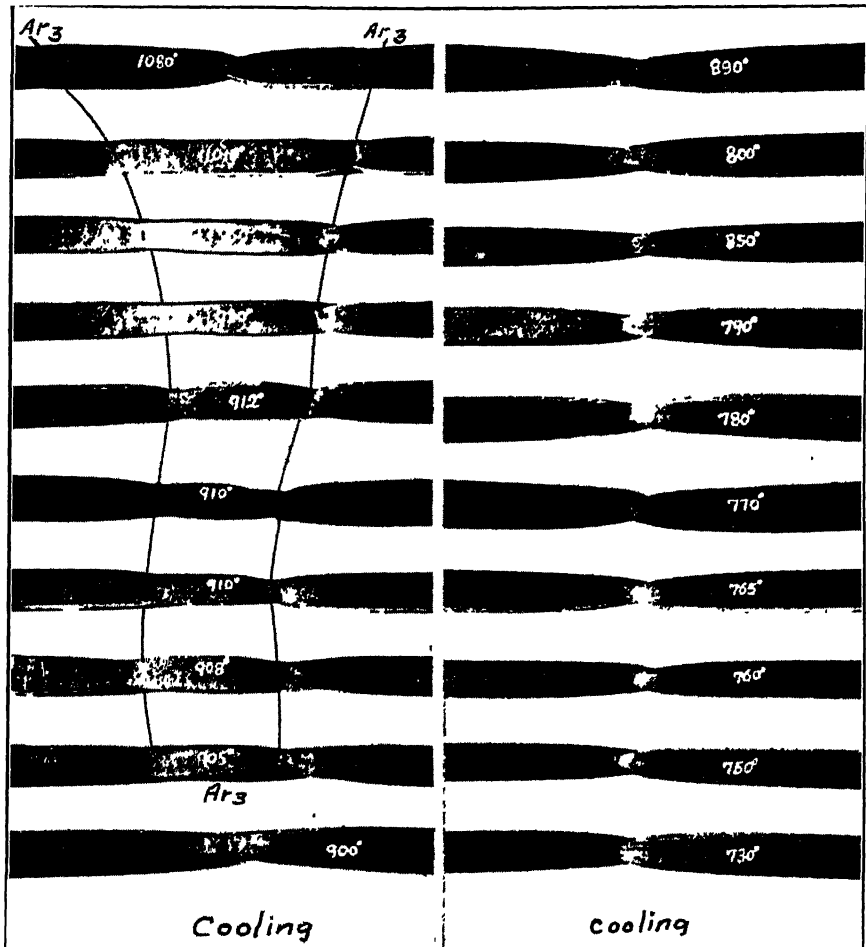


FIG. 12. NORWAY IRON.

higher temperature, resulting, so to speak, in a longer section where fracture must occur, it being known that very short reduced sections yield higher tensile strength results. Corresponding critical points are observed in the elongation and contraction of area curves.

The results obtained in testing, in the same manner, test bars of Norway iron are indicated in Fig. 14. A sharp break in the tensile-strength



curve and in the elongation curve will be found to correspond closely to the  $Ar_3$  point. The horizontality of the curve, once the  $Ar_3$  point is passed, is readily explained. It results from the properties of the metal when it is undergoing its  $Ar_3$  transformation.

The testing of bars of steel containing about 0.50 per cent. carbon yielded similar results, Fig. 15. In this steel, however, the tensile

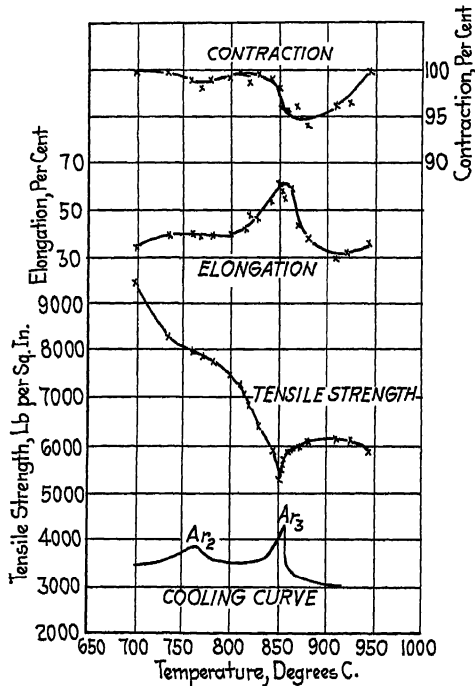


FIG. 13.—TENSILE TESTS OF 0.10-PER CENT. CARBON STEEL UNDER DIFFERENTIAL HEATING.

strength falls steadily after the  $Ar_{3,2}$  point is passed instead of remaining constant. This is due to the fact that the bars are now breaking in the center and therefore at increasing temperatures owing to the absence of critical contractions or critical twists, as clearly revealed by an examination of the bars.

### SUMMARY

Twisting and tensile stresses applied to iron and steel bars heated at the middle to predetermined temperatures, the temperature falling gradually toward both ends of the bars, give the following results:

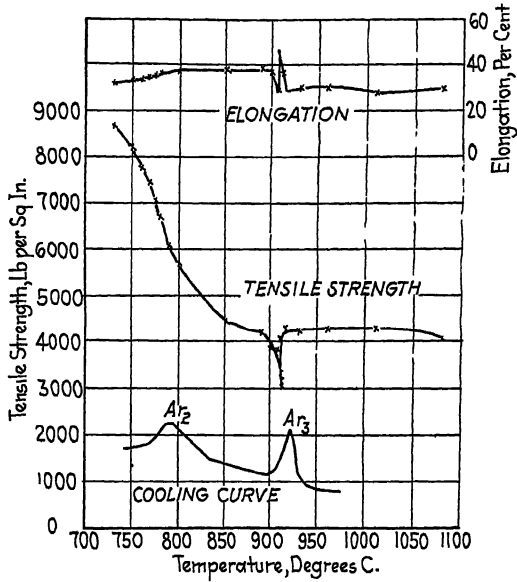


FIG. 14.—TENSILE TESTS OF NORWAY IRON UNDER DIFFERENTIAL HEATING.

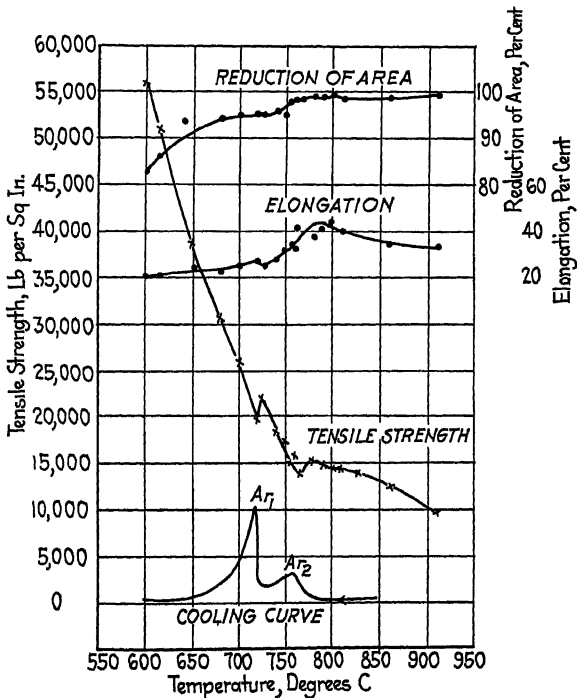


FIG. 15.—TENSILE TESTS OF 0.50-PER CENT. CARBON STEEL UNDER DIFFERENTIAL HEATING.

1. In iron and in steel exhibiting an independent  $A_3$  point, hence in iron and in steel containing less than some 0.40 per cent. carbon, when the bars are heated in the middle to temperatures inferior to that point, they undergo twisting or contraction and final rupture near the center where the temperature was maximum.

When the bars are heated above their  $A_3$  point into a range of temperature which, in carbon-less iron, covers about  $100^\circ$  C. (from  $900^\circ$  to  $1000^\circ$ ), and which is gradually depressed and narrowed as the carbon increases, occurring between  $770^\circ$  and  $800^\circ$  C. in steel containing 0.30 per cent. carbon and being nil when  $A_3$  merges with  $A_2$ , they twist or contract critically and finally rupture at some distance from the center where the temperature was that of the  $A_3$  point.

When the bars are heated above that range they again twist or contract and rupture at the center where the temperature is maximum.

2. In iron-carbon alloys that do not exhibit an independent  $A_3$  point, and, therefore, in alloys containing more than some 0.40 per cent. carbon, critical twists or contractions do not occur, the bars always breaking in the middle.

## The Nature of Martensite

BY EDGAR C. BAIN,\* DUNKIRK, N. Y.

(New York Meeting, February, 1924)

IN STUDYING the structural characteristics of martensite it is desirable that a clear conception of the material from which martensite is produced should first be obtained. Any theory of its formation and structure incompatible with the facts of its parent substance, austenite, can be eliminated with little consideration.

Austenite is the name applied to solid solutions of carbon and other elements in gamma iron. At temperatures above about 900° C. (1650° F.), pure iron exists in a system of crystallinity<sup>1</sup> entirely different from the crystal structure below that temperature. This high-temperature allotrope of iron is of an atomic structure associated with great ductility, having very manifold symmetry and an abundance of easy slip planes. The exceptionally ductile and malleable metals (gold, silver, platinum, copper, aluminum, and nickel) have this same atomic arrangement—the face-centered cubic. The low-temperature allotrope of iron, alpha iron, the solid solutions of which are known as ferrite, has a body-centered cubic arrangement of atoms. Like it, in crystal structure, are the less ductile and malleable metals, molybdenum, tungsten, titanium and chromium. Fig. 1 shows the two atomic arrangements known in iron; the diagrams are drawn to scale.

Either of these modifications of iron may dissolve other elements in the solid state; by so doing, the temperature of the transformation is changed. In general<sup>2-7</sup>, it appears that a solid solvent metal dissolves a metal solute by substituting foreign atoms in its own space lattice. Thus, iron may dissolve nickel in either of its crystalline forms by permitting an atom of nickel here and there to occupy the normal position

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<sup>1</sup> Edgar C. Bain: Studies of Crystal Structure with X-rays. *Chem. & Met. Eng.* (1921) 25, 663.

Arne Westgren: Roentgen Spectrographic Investigations of Iron and Steel. *Jnl. Iron & Steel Inst.* (1921) 103, 303.

<sup>2</sup> Edgar C. Bain: Crystal Structure of Solid Solutions. *Trans.* (1923) 63, 625.

Edgar C. Bain: The Nature of Solid Solutions. *Chem. & Met. Eng.* (1923) 28, 21.

of an iron atom in the pure-iron crystal arrangement. In the case of gamma iron, any number of the points of the iron space lattice may be released to nickel, up to 100 per cent.; it becomes problematical when one should say nickel dissolved in gamma iron or iron dissolved in nickel and it seems logical to choose the 50-50 atomic proportion as the dividing point. In alpha iron, however, only a limited number of the normal iron points of the lattice may be occupied by nickel atoms.

So much has been published recently on the nature of solid solutions that it is, perhaps, unnecessary to point out that the substitution of solute atoms for solvent atoms in the space lattice of the latter seems always to alter the average spacing of the atoms. Large atoms stretch the

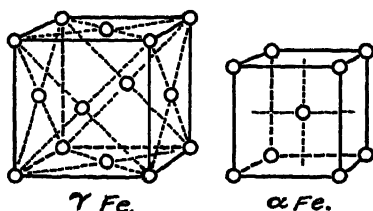


FIG. 1.—COMPARATIVE STRUCTURES OF GAMMA IRON AND ALPHA IRON.

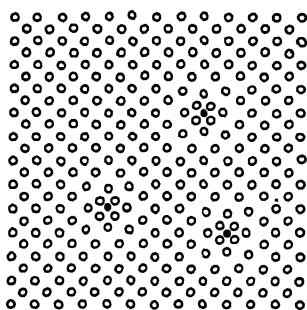


FIG. 2.—POSSIBLE SECTION THROUGH GRAIN OF AUSTENITE ON PRINCIPAL SLIP PLANE, SHOWING DISTORTION OF LATTICE NEAR CARBON ATOM; NOTE WARPED PLANES.

lattice and small ones shrink it; but the unlike atoms seem always to pack more closely than their normal volumes would indicate. The pairs of metals that form solid solutions, but no intermetallic compounds, show the least force (practically *nil*) tending to draw together; while, in general, those pairs with greatest "chemical affinity" show the greatest inordinate shrinkage. The solid solution of any other metal, either soft or hard, brittle or ductile, invariably hardens the metal acting as solvent. The hardening effect seems to depend somewhat on the disparity\* in size of solvent and solute metal atoms and on this chemical affinity as well. We may, with some assurance, assume that the hardness of solid solutions is a matter of the distortion of the space lattice in the vicinity of the foreign atom. At any rate there is indication of definite interatomic forces between unlike atoms in solid solution, whether or not the free

\* A. L. Norbury: The Volumes Occupied by the Solute Atoms in Certain Metallic Solid Solutions and Their Hardening Effects. *Trans. Faraday Soc.* (1923).

Zay Jeffries and R. S. Archer: The Modern Conception of Solid Solutions. *Chem. & Met. Eng.* (1923) 29, 923, 966.

electrons become mutually fixed by this condition, as would be indicated by the increase in electrical resistivity with increase in proportion of solute metal.

Pure iron in the gamma condition can dissolve up to 1.7 per cent. carbon; while in the alpha condition probably not more than 0.08 per cent. is dissolved. When one considers the nature of the atomic arrangement in gamma iron, it is not apparent why carbon can be dissolved up to 7.4 atomic per cent. in gamma iron and so very meagerly in alpha iron. It may be that the ease of finding three iron atoms symmetrically arranged for the carbon atom to hold more or less tenaciously in the face-centered lattice and the complete lack of such possibility in the body-centered lattice has some bearing on the cause of this difference in behavior. At any rate, the great disparity in size between the carbon atom and the iron atom and the strong chemical affinity between these elements will cause marked distortion in the regular atomic arrangement in austenite.

We may then picture a face-centered cubic lattice of iron atoms, with here and there violent distortion around a carbon atom, as the edifice known as a grain of austenite which, on proper treatment, is to rearrange to form martensite or to collapse to produce troostite or sorbite. A section through a principal slip plane of this material is shown diagrammatically in Fig. 2; this may be what could be seen if the atom centers were visible to an "x-ray eye."

In the solution of copper in aluminum, while copper is added to molten aluminum, slow cooling of a 4-per cent. alloy does not throw out copper, but  $\text{CuAl}_2$  is precipitated. From accurate density determinations and atomic space measurements, we are certain that the copper atom is substituting for the aluminum atom in the solid solution, but the compound is precipitated. The material precipitated has no bearing upon the state of existence in the solid solution, as Hoyt<sup>4</sup> has pointed out. Similarly, it is the author's opinion that carbon is atomically dispersed<sup>5</sup> in austenite. The strongest reason for this opinion is the absence of the typical cementite magnetic behavior in wholly austenitic alloy steels containing much carbon, and its immediate appearance after drawing to permit formation of microscopic particles of  $\text{Fe}_3\text{C}$ . The magnetic prop-

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<sup>4</sup> S. L. Hoyt: "Metallography. Metals and Common Alloys," 162. New York, N. Y. 1921. McGraw-Hill Book Co.

<sup>5</sup> While the point is of interest it is not vital to our theories of solid solution. All alloys of metals in metals so far studied seem to be atomically dispersed in the manner described but it seems likely that when a compound of metal and non-metal dissolves in a solid metal there may be a substitution of a molecule for an atom. Thus  $\text{Cu}_2\text{O}$  in Cu probably forms by having a  $\text{Cu}_2\text{O}$  molecule occupy the ordinary normal Cu point. The oxygen atom probably is carried along with the copper much as the electrons are carried by the nucleus. It is possible, too, that  $\text{PdH}_2$  enters into the Pd lattice substituting for a Pd atom.

erties of a material are so subtly connected with the molecule itself that were  $\text{Fe}_3\text{C}$  present even in single molecules, we would find it difficult to explain the absence of the  $200^\circ \text{C}$ . ( $390^\circ \text{F}$ .) magnetic phenomenon. The exact condition of carbon in austenite, however, is not vital to this study.

In the decomposition of austenite there are, in the main, two feats to accomplish. The one is the elimination of dissolved carbon, for the carbon becomes gradually less soluble down to  $700^\circ \text{C}$ . ( $1290^\circ \text{F}$ .) and very abruptly almost insoluble below this temperature; the other is the transformation of gamma iron to alpha iron. These two phenomena are intimately inter-related but may, for convenience, be considered separately. Indeed, martensite immediately after formation represents the product of the change from the gamma to alpha condition of the iron with the carbon entirely unmolested as to position and association by the action.

It is perhaps instructive to contemplate the nature of carbon-iron alloys, if there were no alpha modification of iron.<sup>6</sup> We should have the solidus line of our diagram as at present. The junction of the  $A_{cm}$  line with this solidus at  $1075^\circ \text{C}$ . ( $1970^\circ \text{F}$ .) and 1.7 per cent. carbon would, of course, mark the upper end of a much longer  $A_{cm}$  line extending to a very small carbon concentration indeed at room temperature.

We should have a heat-treating schedule for this hypothetical steel very similar indeed to that of duralumin, except for actual temperatures. The material would be heated to dissolve most of the cementite for forging; the quench would be from a temperature that would leave some carbide particles to inhibit excessive grain growth, this quenched solid solution would be relatively soft. To harden, the steel would be drawn to a temperature allowing for the unstable solid solution to precipitate the excess cementite in critically sized particles for keying the austenite slip planes. This temperature would be such as, in the time allotted, would increase the mobility of the atoms to an extent permitting crystallization of cementite of optimum grain size. Such a material might have very desirable properties and, while not so hard as martensite, would probably have a Brinell hardness of 500-550.

The complication of the abrupt change in crystal structure of iron, with its attendant sudden change in solubility for carbon, has made the mechanism of hardening of steel vastly harder to understand. In pure iron, there is no known method of preventing, or even retarding, the allotropic change at  $900^\circ \text{C}$ . ( $1650^\circ \text{F}$ .). On heating iron (in the alpha condition) to this temperature, a complete recrystallization takes place. New grains form and grain growth is rapid. If this gamma iron is cooled, a new set of grains of new orientations form which also grow rapidly. There is reason to believe that the number of nuclei from which either

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<sup>6</sup> S. L. Hoyt: *Op. cit.*, 147.

the gamma or the alpha grains begin to grow is not relatively large. At any rate, heating quickly just above 900° C. (1650° F.) and instantly quenching with utmost severity suffices to produce only a moderate refinement of grain. This refinement of grain and concurrent resistance to slip by end obstruction is not sufficient to cause an increase of hardness in pure iron at all comparable with that of the grain "fragmentation" of cold work.

We could expect only this condition. The temperature for the alpha-gamma transformation in pure iron is so high that it is not only above the recrystallizing temperature for cold-worked iron but is in a range for very rapid grain growth. With no obstructing material and a few nuclei, ideal conditions are provided for good grain size even in the briefest time; but with the presence of dissolved carbon in the gamma iron or austenite, we have very different circumstances.

As regards grain refinement the result of even low-carbon steel is very different from that of pure iron. Two tendencies are at work to cause this. The temperature for grain growth is raised by the addition of even a small amount of a dissolved metal; hence grain growth in austenite is retarded by the presence of carbon. This carbon also tends to lower the temperature of the transformation, causing it to occur accompanied by much less atomic mobility. If the carbide has precipitated at once in the new small ferrite grains, their growth is enormously retarded by its presence. Any discontinuity in a metal affords a local inhibition to grain growth.

It is not surprising, then, that at as low carbon content as 0.20 per cent., by extremely rapid cooling an almost entirely distinct appearance in the carbon-iron alloy is obtained. The characteristic acicular structure is seen under the microscope; and by the quench into iced brine, the austenite has changed to a material with twice the Brinell hardness number of the annealed alloy. Higher carbon content gives increasingly greater hardness by this treatment; to such material the name martensite has been given.

The hypoeutectoid steel has been considered, in the foregoing paragraphs, to stress the vast effect of even a little carbon in the structure obtained. In the further discussion, reference will, in general, be made to iron-carbon alloys of higher carbon content, such as tool steel. In considering causes of hardness, the author utilizes the convenient conception of the mechanism of hardening known as "slip interference theory of hardness"<sup>7</sup> originally touched on in a small way by Henry M. Howe and later amplified and adapted for general usefulness by Jeffries and Archer. An explanation for hardness might be found in the existence of: (1) a solid solution wherein the solute exerted much distortion on

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<sup>7</sup> Zay Jeffries and R. S. Archer: The Slip Interference Theory of the Hardening of Metals. *Chem. & Met. Eng.* (1921) 24, 1057.



the lattice, (2) extremely fine grains or grain fragments, (3) hard particles of critical size to key slip planes. For ordinary martensite, we would choose the second possible cause with much less information than that which is now available.

As a matter of fact, the author demonstrated, by computing the amount of diffusion occasioned in the diffracted beam of monochromatic  $x$ -rays by different sized crystals, that martensite even when formed from coarse austenite is extremely fine-grained; possibly perfect crystallinity does not extend over a distance greater than 50–100 atom rows. Inasmuch as we know of no other material in all metal practice consisting of such grain size or effective grain size, it is difficult to say whether or not this property alone of martensite is responsible for all the hardness, but certainly it is the main cause of its excessive hardness.

In any case, except the most drastic quenches of the higher carbon iron-carbon alloys, the martensite is wholly alpha iron. For this information we are practically forced to accept the results from  $x$ -ray diffraction.<sup>8</sup> We must probably conclude that freshly quenched martensite is essentially extremely fine-grained ferrite. But having noted that the allotropic change has been accomplished in the formation of martensite, what of the carbon?

To Portevin and Garvin<sup>9</sup> and to Chapin,<sup>10</sup> we owe much for throwing light on the sequence of the changes in hardening steel. They have proved conclusively that martensite, at least in most steels, including alloy steels, forms at low temperatures. The formation of martensite appears to depend on lowering the temperature of the austenite so quickly below 600° C. (1110° F.) or perhaps 550° C. (1020° F.) that lessened atomic mobility cannot permit the diffusion of carbon in the mass to form Fe<sub>3</sub>C. Indeed, the work just referred to shows that by very rapid quenching to 200° C. (390° F.) or 300° C. (575° F.) a hypereutectoid steel may be retained austenitic for several minutes, after which it becomes martensitic. If any considerable time is permitted in the cooling from the austenite condition to 100° or 200° below the critical, there is sufficient

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<sup>8</sup> At the same time that martensite was being studied by the  $x$ -rays, low-carbon steel was held at a great variety of temperatures while the diffraction pattern was recorded. The iron samples were heated by electric current and protected from oxidation by an argon atmosphere or the samples were made to form the filament in tiny incandescent lamp-tubes very transparent to  $x$ -rays. By either method no pattern other than that of ferrite was obtained below the  $A_1$  temperature. This body-centered form was recorded for the beta-iron range. These results were obtained independently by Westgren in Sweden. Further, no allotrope of iron was found for the blue-heat phenomenon, only alpha iron was found for this range.

<sup>9</sup> A. M. Portevin and M. Garvin: The Fundamental Investigation of the Influence of the Rate of Cooling on the Hardening of Carbon Steels. *Jnl. Iron & Steel Inst.* (1919) 99, 469.

<sup>10</sup> W. R. Chapin: Properties of Some Steels in the Hardening Range. *Trans. Am. Soc. for Steel Treat.* (1922) 2, 507.

atomic mobility for carbon migration so that troosite may form without any martensite whatever; this point will be taken up later. Chapin finds that these alloys expand continuously until wholly martensitic, whereupon they contract as they become troostitic or sorbitic. It is on this circumstance that we can base our belief that freshly quenched martensite is without any cementite particles. For cementite is the most dense of the constituents of steel and on formation increases the density (sp. gr.) of steel nearly to what it was in the austenitic condition. Ferrite is least dense. Hence, the minimum density marks the complete destruction of austenite and the earliest stages of cementite precipitation. With carefully prepared martensite, Honda<sup>11</sup> has been able to establish the absence of cementite just as in austenite and to cause its appearance magnetically by heating to 300° C. (575° F.). We may now amplify our definition of martensite by including carbon atomically dispersed in extremely fine-grained ferrite. The size of the ferrite grains is certainly in the colloid range.

But this freshly quenched martensite is not a commercial material and is most ephemeral. At room temperature, cementite begins to precipitate out at a decreasing rate; at higher temperatures it precipitates more rapidly. Fortunately this precipitation does not continue to occur to form supercritical sized particles at room temperature. The outstanding characteristic, perhaps, of martensite is the complete allotropic change from gamma to alpha iron and the completely suppressed precipitation of carbide.

Some of the above conceptions regarding martensite have been set forth by Jeffries and Archer<sup>12</sup> who have discussed these points in considerable detail. The present author will present his views regarding a possible mechanism of the martensite transformation.

It is reasonable to suppose that the iron atoms in austenite rearrange with no difficulty at all in pure iron to form ferrite. We are familiar with the speed with which the cold-worked grain fragments are wholly recrystallized on the annealing of pure metals after being drawn or rolled into wire or sheet; indeed they may almost flash into large grains. But the allotropic rearrangement of iron at 300° C. (575° F.) or lower is not likely to be accomplished in the same easy manner; the spacings are more rigidly preserved. With carbon present, we know that the austenite is enormously stabilized; therefore, it is a reasonable assumption that the portions of an austenite grain most remote from carbon atoms will form the nuclei for the transformation and that those regions having the lowest concentration of carbon atoms for any reason will transform first.

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<sup>11</sup> Kôtarô Honda: On Magnetic Analysis as a Means of Studying the Structure of Steel. *Jnl. Iron & Steel Inst.* (1918) 98, 375.

<sup>12</sup> Zay Jeffries and R. S. Archer: The Hardening of Steel. *Trans. Am. Soc. for Steel Treat.* (1923) 263-304.

There may even be a small tendency for carbon to recede some distance from the first alpha iron nucleus, thereby enriching slightly the remaining austenite. This would explain the interesting findings of Hanemann<sup>12</sup> as to carbon content of martensite and adjacent austenite. It is reasonable, also, that the atoms themselves will rearrange with the greatest possible facility by a method that will require the least temporary distortion; we cannot expect an atom to squeeze through some narrow spacing, for instance. A mode of atomic shift requiring minimum motion was conceived by the author some months ago and was later discussed with Dr. Ancel St. John who, in the meantime, had thought of the same scheme of things and accepted it as highly probable. It is not

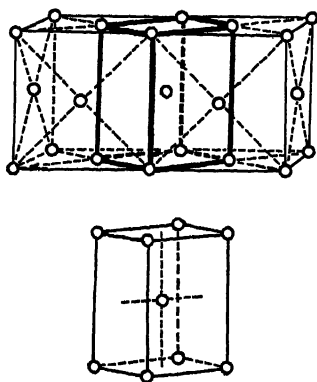


FIG. 3.—BODY-CENTERED TETRAGONAL LATTICE DELINEATED IN AUSTENITE (FACE-CENTERED CUBIC) STRUCTURE.

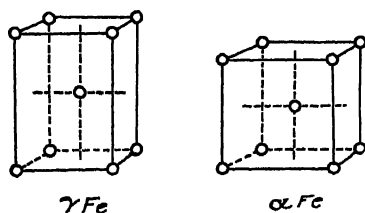


FIG. 4.—BODY-CENTERED TETRAGONAL LATTICE OF AUSTENITE AND BODY-CENTERED CUBIC LATTICE OF ALPHA IRON PRODUCED BY "UP-SETTING" THE FORMER; DRAWN TO SCALE FOR COMPARISON.

surprising that this should have occurred, as it is the only easy method of constructing a body-centered atomic structure from the face-centered cubic crystal.

In Fig. 3 is shown a portion of an austenite lattice. If one regards the centers of faces as corners of a new unit, a body-centered structure is already at hand; however, it is tetragonal instead of cubic, as seen in Fig. 4. Thus austenite might equally well be spoken of as a body-centered tetragonal crystal with axial ratio 1.414. The dimensions of this crystal unit are approximately 3.592 Angstrom units height (0.000000141 in.) by 2.54 Angstrom units edge (0.0000001 in.). To form alpha iron, this body-centered square prism must shorten from 3.592 Angstroms to 2.86 Angstroms in height and simultaneously expand in edge from 2.54 Angstroms to 2.86 Angstroms. Fig. 4 shows, to scale,

<sup>12</sup> A splendid account of the retention of distinctive coloration of austenitic and martensitic areas after drawing by Hanemann is given in Hoyt's "Metallography: Metals and Common Alloys," 166.

this change. There are three axes in the austenite grain on which this change may take place by the "upsetting" procedure just indicated. This procedure must give a very fine grain in the alpha condition after transformation, else the martensite will fall to a powder. Suppose that there is a succession of lattice points pressing together along one axis and opening up in the other two. Unless this movement is compensated by encountering soon the opposite state of affairs along any given direction a rupture would ensue. This procedure would probably account for a structure consisting of plates and spars, but it is not to be supposed that the long needles one sees in an austenite-martensite mixture are wholly of one orientation. These needles might represent the path taken by this alternate compression and extension movement. Tremendous forces tending toward rotation would accompany any progression of this change along an austenite axis. Accordingly the unchanged austenite islands in the course of martensitization would doubtless be turned about, and likewise fragments of martensite might also be twisted. If this were not the case we should find only a few orientations of ferrite in a single austenite grain after transformation; this most certainly is not the case. That this compensating action is in effect may be inferred from the fact that the old austenite grain boundaries are often fairly well preserved after the change; but that there are also extensions and compressions locally developed is shown by the roughening of a polished surface of austenite after martensitization is brought about by cooling to liquid-air temperatures.

It is the author's opinion that, in martensite, there is a vast amount of very poorly crystallized material having warped planes and such imperfections. With so many nuclei in a material of such rigidity, the last austenite to rearrange imperfectly between two crystallites of alpha iron must find that a compromise for its atom positions is necessary, to conform to the directional forces from both grains. Furthermore, in these regions last to change, the carbon atoms are most plentiful and they would further resist perfect crystallinity. There is probably a greater proportion of this so-called amorphous material of low crystallinity present in martensite than in any other known metallic aggregate, including cored crystals. At low temperatures, such an arrangement of atoms would be very hard indeed; it would also be a structure that would begin to recrystallize at low temperature.

It is interesting to note that in high-carbon steels there is a range of minimum rate for the allotropic change to take place if the austenite has been safely brought down through the normal temperature for change at 700° C. (1290° F.). The austenite-martensite change is quite sluggish between room temperature and 350° C. (660° F.). Cooling to liquid-air temperature or heating above this range accelerates the change enormously. The rate of change in very high-carbon steel

is so slow that the author has frequently found by  $x$ -ray analysis a good proportion of austenite present after many weeks in ordinary carbon steels.

In this connection, it may perhaps be fitting to suggest that a danger lies in using our words too loosely as applied to the structural constituents of steel. As an example, in high-carbon steel, freshly quenched, a good portion of austenite seems to be retained. However, the author would question the statement, "The martensite microstructure indicates the existence of a mixture of alpha- and gamma-iron crystals, the proportion of gamma-iron crystals decreasing and the proportion of alpha-iron crystals increasing as the structure approaches the troostitic," found in Zornig's "Examination of Steel by the X-ray Spectrometer." Of course, this mixture might have been named martensite but to use this word arbitrarily for this mixed condition would confuse our description in literature hopelessly. The author finds that this gamma-alpha mixture is softer than the "de-austenitized" martensite resulting from a liquid-air treatment. Further, the acicular structure is plainly seen (especially in lower carbon steel) when the iron is wholly alpha. It would appear doubtful that we can include any gamma iron as a necessary part of martensite. Great care should be exercised to stabilize the language of steel treating.

It appears that at temperatures nearly as high as the critical, tiny cementite particles can be precipitated simultaneously with, or even partly ahead of, the allotropic gamma-alpha transformation. Thus troostite is formed without the formation of martensite. If, however, the carbon has not been allowed to migrate and concentrate to form such crystallites at the time of the transformation of the iron structure, martensite is formed. It then proceeds to throw out cementite at once (even at room temperature) and at higher temperature the cementite becomes of sufficient grain size to form troostite; this latter method is the usual procedure in forming troostite. It appears that troostite is merely fine ferrite with cementite particles of a certain size range precipitated therein. This size is supercritical on the one hand (troostite being always softer than martensite) and not large enough to slow up solution in acid on the other hand. It seems possible the cementite particles act as the cathodes in a myriad of tiny cells when steel is dissolved in acid. If these tiny spots for hydrogen evolution are too far apart, the action is retarded. If the carbon is atomic or combined in molecules of a very small number of atoms, it appears to protect the iron from acid attack. The maximum action takes place at some intermediate size; this region results from a troostitic state.<sup>14</sup> As the particles grow larger, we have the sorbitic and finally the spheroidized cementite conditions with a smooth succession of lower hardness values.

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<sup>14</sup> S. L. Hoyt: *Op. cit.*, 179.

To summarize, we have:

*Austenite*, a face-centered, cubic, gamma-iron lattice with carbon in solid solution. Carbon atoms probably, although not positively, occupy normal iron points in the space lattice. This structure is stabilized by carbon particularly when retained in an unstable condition at temperatures between room temperature and 350° C. (660° F.).

*Freshly quenched martensite*, not important; only a transient condition. Extremely distorted and fine-grained ferrite grains (equivalent to 50–100 atom rows in size) in which carbon is mechanically held in atomic dispersion, a pseudo-solid solution. Probably this substance contains much amorphous or badly crystallized iron.

*Martensite*, extremely fine-grained alpha iron, but with some carbon associated with iron to form  $\text{Fe}_3\text{C}$  in particles not larger than the critical size in extent.

*Troostite*, somewhat larger, and much more perfectly formed crystals of ferrite in which supercritically sized particles of  $\text{Fe}_3\text{C}$  are precipitated.

*Sorbite*, same as troostite but with further growth of ferrite grains and  $\text{Fe}_3\text{C}$  crystallites or particles. These  $\text{Fe}_3\text{C}$  particles are probably not far from 1000 atom rows in diameter.

Unfortunately, it is probably true that the occurrence of the magnetic change in iron so near the temperature of the atomic rearrangements, and concomitant abrupt change in carbon solubility, has actually served to obscure the mechanism of the hardening of steel. Occurring in this range, explanations for both effects were attempted most logically; whereas in all probability the abrupt change in magnetism is due to some cause within the atom which might, so far as atomic arrangement is concerned, have occurred at any other temperature. However, new means of study invariably open up new problems and it may be necessary to know of these changes within the atom that cause allotropy, etc., in which case we will probably find that all of the phenomena of heat treatment are results of subtle alterations in relations of electron and nucleus.

## DISCUSSION

ANCEL ST. JOHN, New York, N. Y.—As the author has said, he and I independently, and almost simultaneously, reached the same conclusions as to the mechanism of the transformation from austenite to martensite but his able presentation of the idea leaves little to be said. It appeared to be of interest, however, to prepare some models, using cork balls to represent the location of atom centers and needles to join an atom center to its nearest neighbors.

In Fig. 5, the small model on the left-hand side represents fourteen atoms, forming a face-centered cubic group characteristic of gamma iron.

The small model on the right represents nine atoms, forming a body-centered cubic group characteristic of alpha iron. The large model on the right represents thirty-five atoms, forming a larger cubic group of the body-centered type, as emphasized by the nine black balls. The large model on the left represents the same number of atoms at the same distances from their nearest neighbors, but enough closer together hori-

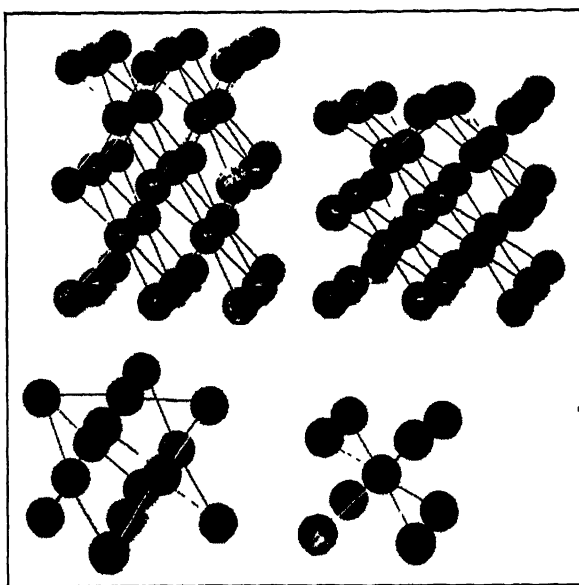


FIG. 5.

zontally and farther apart vertically to bring them into the face-centered cubic arrangement, as emphasized by the fourteen black balls, while preserving the body-centered characteristic in the tetragonal instead of the cubic form. The two structures, gamma iron on the left and alpha iron on the right, are similar except that the gamma iron is longer and more slender.

For some reason, which we do not understand, iron atoms when sufficiently agitated, *i. e.*, at high temperatures, prefer to arrange themselves in the form shown on the left; at low temperatures in the form shown on the right. In passing from the one temperature zone to the other, whether during heating or cooling, the atoms will tend to change their arrangement. A little consideration will show that the transformation can scarcely take place throughout each grain uniformly, for stresses will be set up by the considerable dimensional changes involved sufficient to cause local rupture. The original grains will disintegrate spontaneously

into a lot of small "grainlets," making a sort of granitic mass. Carbon atoms present points of incipient stress and will tend to promote the transformation, thus decreasing the degree of agitation required or lowering the transformation temperature, and at the same time will tend to increase the degree of fragmentation.

It is of interest to consider what may happen in a particular instance. In the face-centered cubic arrangement each atom is surrounded by twelve others equidistant from it. If one of such a group of atoms is carbon and the other twelve are iron, the composition will be  $\text{Fe}_{12}\text{C}$  or 0.176 per cent. carbon. This suggests a structure for saturated austenite. If for reasons best known to themselves the carbon atom and three iron atoms, at a certain temperature, separate from the group to form a little group  $\text{Fe}_3\text{C}$  of their own  $\text{Fe}_9$  will remain. But  $\text{Fe}_3\text{C}$  is suggestive of cementite and  $\text{Fe}_9$  is suggestive of the body-centered cubic grouping in ferrite, and it may be that the secret of the true relationships of austenite, martensite, cementite, and ferrite is to be found in these very facts.

HENRY S. RAWDON,\* Washington, D. C. (written discussion).—One of the most important points in the author's premises is the assumption that pure iron cannot be hardened by simple thermal means, as can the iron-carbon solid solution. The statements, on pages 28 and 29, to this effect require correction. Pure iron, at least iron of the purity of the electrolytically deposited variety (0.02 per cent. carbon) can and has been hardened by thermal means; moreover the degree of hardness produced is far greater than can be produced by cold working.

To do this, the heat must be concentrated on a tiny mass of metal and it must be cooled with extreme rapidity. This can be accomplished, with ease, by using a small pencil of the iron as one contact and a polished block of the iron for the other contact of a high-potential spark gap. An electric "stylograph," such as is used for writing on metals, is admirable for the purpose. By means of the electric spark, a very small volume of iron is heated above its fusion point ( $1530^\circ \text{C.}$ ) and cooled immediately; the rate of cooling is exceedingly rapid. No attempts have been made to measure the rate, even approximately, in the experiments that have been carried out from time to time at the Bureau of Standards. However, the finger tip can be placed upon the spot immediately after the spark has passed without any feeling of discomfort.

To what extent the allotropic transformation in the iron is suppressed or interfered with by this rapid cooling is entirely a matter of speculation. The fact, however, that iron heated and cooled in this way is very hard, can be readily demonstrated by measurements made by the scratch-hardness method, the test being carried out after very light grinding and polishing of the "sparked" surface of the specimen.

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\* Physicist, Bureau of Standards.



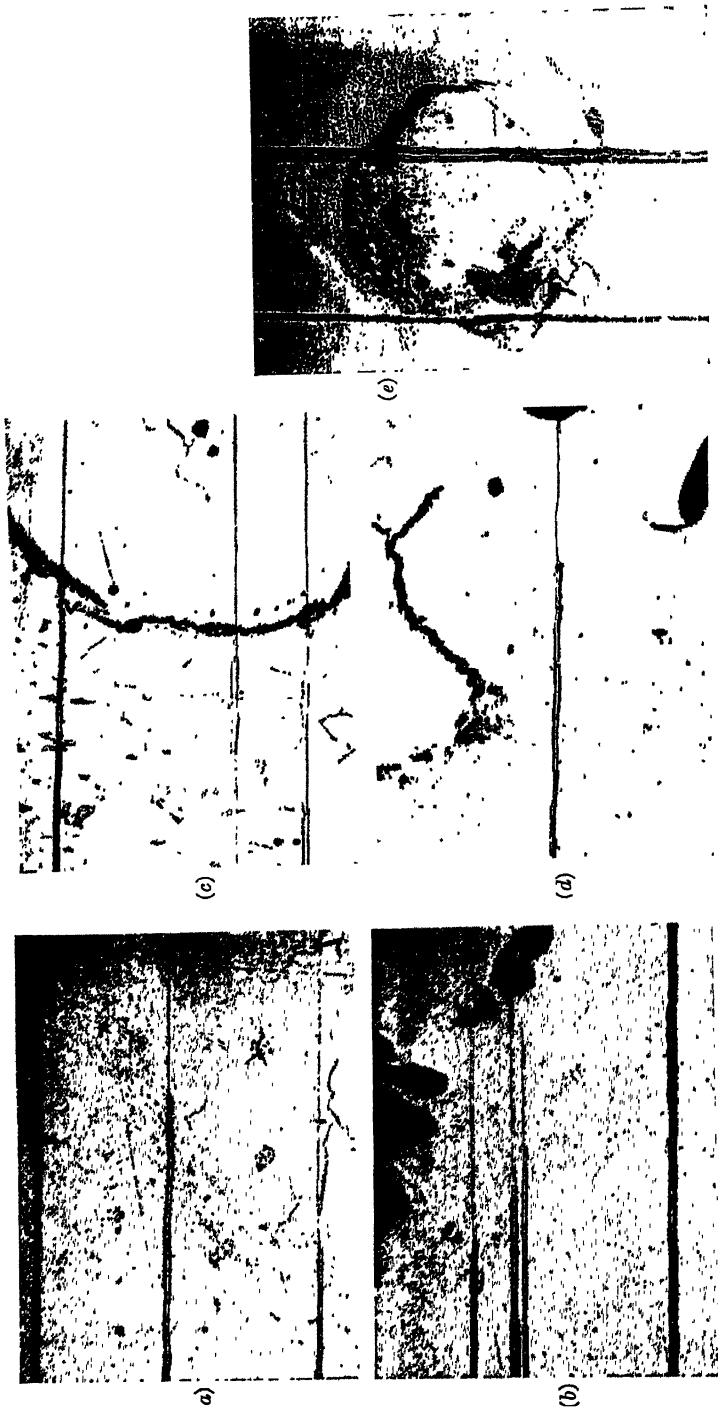


FIG. 6.—SCRATCH HARDNESS MEASUREMENTS DEMONSTRATING THE EFFECT OF HARDENING TREATMENT BY USE OF ELECTRIC SPARK ON IRON, SOFT STEEL, AND NICKEL.  $\times 100$ . (a) Electrolytic iron. (b) Similar to (a) evidently cooled at a slightly slower rate as evidenced by the absence of cracks in the sparked area, such as are seen in (e). (c) 0.07-per cent. carbon steel. (d) Same as (c) tempered at  $200^{\circ}\text{C}$ . for 30 min. (e) Electrolytic nickel; sparked area has same hardness as surrounding or untreated portion. (a), (b) and (c) etched with picric acid before scratch was drawn; (d) and (e) unetched.

It is very essential when conducting these experiments that the two contacts be of pure iron in order to eliminate all possible chance for contamination of the fused spot.

Electrolytic nickel when sparked in a similar manner, an electrode of nickel being used, gave quite different results. Although the metal was heated above its fusion temperature ( $1452^{\circ}\text{C.}$ ) and cooled as rapidly as before, thus giving an exceedingly fine grain, no measurable difference in scratch hardness was detected in the "sparked area" as compared with the rest of the surface of specimen. Copper, when suitably "sparked," gave results analogous to those obtained with nickel. The conclusion is obvious: the gain in hardness of the iron must be attributed to the allotropic change characteristic of this metal. The photomicrographs in Fig. 6 illustrate results obtained in this manner. As might be expected, the addition of a small amount of carbon aids in the hardening of the iron. Steel of 0.07 per cent. carbon, when fused by sparking and cooled immediately, has a hard glasslike surface over which the jewel point of the scratch-hardness instrument glides without making any appreciable cut. These results are presented, not for discrediting in any way the author's excellent discussion, but rather for emphasizing what appears, to the writer, to be the most essential point of the paper. The results obtained in the experiments on the sparking of iron are not extensive enough to warrant much speculation. However, if one were to venture an explanation of the nature of martensite, on the basis of these results, it would be one that would amplify and emphasize the author's suggestion (page 33) when he states that "in martensite there is a vast amount of very poorly crystallized material having warped planes and such imperfections." Carbon does not seem to be fundamentally essential in the hardening process although it is a powerful adjunct. Whether grain size is to be considered as one of the essentials depends of course on the definition and concept of this term.

JEROME ALEXANDER, New York, N. Y.—Some of the views presented might be explained along the idea advanced a number of years ago by Prof. Theodore W. Richards, which is that atoms are compressible. We commonly have been speculating on and dealing with atoms as though they always had one fixed size, whereas Richards showed quite conclusively that atoms are to be regarded as compressible.

Another difficulty that always confronts us in matters of this kind is the difficulty in deciding when we have solid solution and when we have chemical combination. With all due respect to the  $x$ -ray spectographic evidence, I hardly see how that is going to be conclusive, for it is pretty generally conceded that sodium chloride is a chemical compound and yet the  $x$ -ray spectrometer shows an absolutely definite crystal lattice. Are you going to consider sodium chloride a solid solution of chlorine and sodium? In other words, where are you going to draw the line

between solid solution and chemical combination if you reduce down to atomic dimensions?

It is just one way of looking at the facts. Take the case of austenite: Apparently the *x*-ray spectrometer shows that we have carbon atoms dispersed. Somebody went so far as to say that there is no such thing as a molecule of sodium chloride, that the whole crystal of sodium chloride is the molecule with billions upon billions of atoms of each kind in it.

In a question of this kind we can learn a great deal by taking analogies that are even a little clearer than the cases referred to here in iron; for example, the dispersions of gold in glass, which can be followed ultramicroscopically and also with the *x*-ray spectrometer. Generally speaking, it may be said that dispersions of gold, which are too fine to be seen even in the ultramicroscope, show the definite crystal lattice of gold. Scherer did that work some time ago on aqueous gold dispersions.

Take a piece of transparent ruby glass: they call it "colorless ruby glass," because in making ruby glass you first dissolve gold in the glass and then, by a gradual reheating, allow the particles of gold to grow until they become ultramicroscopically visible, and that is what gives the glass the red color. In other words, the glass is colorless until the little crystals of gold have grown to a size where they are visible in the ultramicroscope; then the color gradually develops. Way below microscopic dimensions, however, there are apparently crystal nuclei formed; and as a consequence, the chilling of the ruby glass will control the number of little particles of gold that are in it. When there are a very large number of small crystals of gold the color of the glass will be a beautiful ruby color; whereas, if the original chilling is of such a nature that there are fewer nuclei, but larger ones, when tempered the finished glass will have a smaller number of large gold particles, which gives the glass a dirty violet color, sometimes running into a brownish color and spoiling it as ruby glass.

I will repeat these points: First, atoms are compressible, and there is no reason why, as the temperature drops, the atoms should not squeeze together and actually occupy less space and even shift their positions. Then comes the question as to where we are to draw the line of demarcation between solid solution and chemical combination; it is questionable whether we are going to be able to draw a sharp line in that particular case. Also there is the question of the analogy between what happens in metals and what happens throughout nature.

The fact that martensite is the hardest phase that we meet in all the forms of steel is quite coincident with a whole series of phenomena that we find generally throughout colloidal dispersions; that is, there is a zone where maximum colloidal properties are distributed. The basic principle underlying this seems to be something of this nature: The specific surface

(by which I mean the total free or exterior surface per gram figured on the basis that you have spheres to deal with, which of course is only approximately true) will plot as a hyperbola against decreasing particle size.

Another factor is the kinetic motion of particles. That ordinarily starts at about zero with particles one micron in diameter and slowly increases until the kinetic motion rises with great rapidity. Langmuir told me, I think, that theoretically the motion of a molecule of gaseous hydrogen was in the neighborhood of 4000 ft. per sec. So that those two curves will cross, which means that where the particles are larger than colloidal dimensions the free surface is rather small but the kinetic motion is practically zero.

When the particles approach molecular dispersion, the free surface becomes enormous and ordinarily would hold the particles fixed, as a result of the play of surface forces; but the kinetic motion in all aqueous dispersions where the particles are free to move is so great that it overpowers any tendency of the particles to hold together. Between those two extremes is the zone of maximum colloidal effect, where there is a balance between free surface and kinetic motion.

You may say that in metals there is no kinetic motion. Roberts-Austen laid sheets of gold and lead together and found they diffused together if given sufficient time. I do not see why similar things cannot happen here (that is, atomic migration to a very minute extent) although perhaps not in steel.

ANCEL ST. JOHN.—If we could imagine the existence of a continuous solid solution of sodium in chlorine in various proportions, we could think of the special case in which we have fifty-fifty proportions atomically, as having an arrangement such as is characteristic of sodium chloride as we know it; that would be the intermetallic compound  $\text{NaCl}$ , but there would be the continuous series of solutions of sodium and chlorine on both sides of it.

We can think, in the same way, of the case of solid solutions, for instance, of nickel in iron. You can add nickel to iron up to certain proportions, but at a certain composition (which happens to be one nickel atom for every three iron atoms) an entirely different crystalline habit appears and you go on with the solid solution of what now is really iron and nickel. That one case of  $\text{Fe}_3\text{Ni}$  you could consider as an intermetallic compound, but there are cases where you do not have any range of solid solution at all but where you do get intermetallic compounds.

It is correct, from one point of view, to say that a crystal of sodium chloride is the molecule of sodium chloride, because it is absolutely impossible to pick out some atoms and say, "This sodium and this chlorine belong together and all others are ranged similarly." You cannot pick out any one particular group. But if you take  $\text{Al}_2\text{O}_3$ , you can pick out particular groups of two aluminum and three oxygen atoms and those

groups repeat themselves over and over again to form the structure. That brings out the point of distinction between a continuous structure and a structure of groups. The thing that would be the molecule would be the smallest structure which, repeated over and over again, would give us the entire large structure.

Thus, we are right in saying that sodium chloride is NaCl because you can take one sodium atom and one chlorine and repeat this group over and over, and get the whole structure. That, probably, is the most sensible point of view in regard to what constitutes the molecule in inter-metallic compounds, or solid solutions, or whatever you please, if you want to talk of a molecule.

The same considerations apply to steel as to ruby glass; in fact, the author has measured the dimensions of colloidal particles in martensite and has found them to be of dimensions that lie within the colloidal range. I have carried other materials through from only ten atoms in diameter up to where they were of microscopic visible size.

JEROME ALEXANDER.—I am pleased to hear that martensite was at about the point of maximum colloidalilty; Professor Benedicks, of Sweden, claimed that colloidal dimensions only appeared in troostite.

EDGAR C. BAIN.—The change is continuous.

JEROME ALEXANDER.—I am quite positive that he said colloidal dimensions only began with troostite. I differed with him on that, not so much from the metallurgical standpoint as by reasoning that nature is not going to do anything unusual with metals.

HOWARD SCOTT, Washington, D. C. (written discussion).—Steel is a unique alloy in that it behaves both as a binary alloy whose components are insoluble in the solid state and as one whose components are soluble in the solid state, the system followed depending only on the cooling rate from the critical point. We are indebted to the author, and others, for the final and conclusive proof that the product of fast cooling, martensite, is a true solid solution. The possibility of this fact has long been suspected, but it remained for *x*-ray analysis to produce conclusive evidence of its truth. This finding clarified our knowledge of hardening, but it also introduced new problems.

One of these problems, which is attacked by the author, is the cause of the extreme hardness of martensite. He follows Jeffries and Archer in ascribing the hardness of martensite to a critical submicroscopic grain size indicated by *x*-ray analysis. This hypothesis assumes that the grain size is quite independent of the quenching temperature and the cooling rate for these variables have little effect on the hardness of martensite. Rawdon and Epstein have shown<sup>15</sup> that the hardness of martensitic carbon steels are not materially affected by the quenching temperature.

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<sup>15</sup> Bureau of Standards *Sci. Paper* 452.

It has been shown that the cooling rate during the hardening transformation has little effect on the hardness of martensite.<sup>16</sup> The experiment was as follows: Several specimens of an oil-hardening steel were quenched simultaneously in oil and withdrawn just before the hardening transformation was reached. They were then cooled at different rates to room temperature. The values of the hardness obtained with the Rockwell diamond-cone test differed by less than 5 per cent. between the

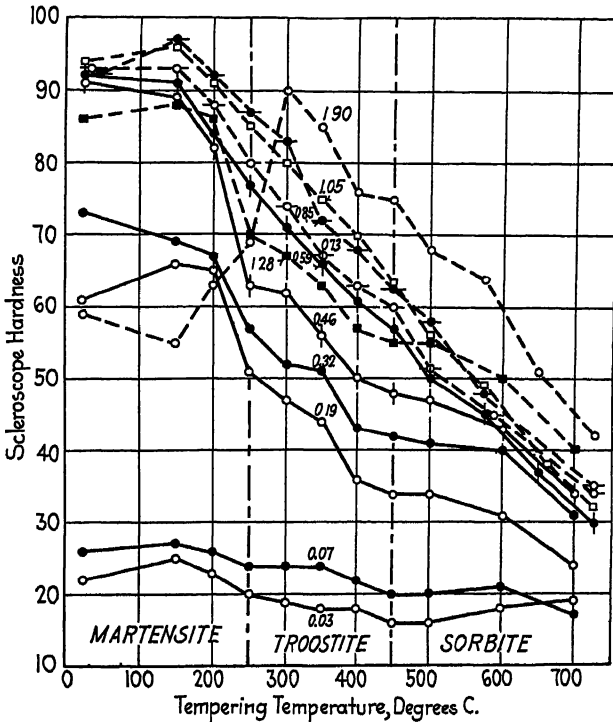


FIG. 7.

extreme limits of the final cooling rates used, namely air cooling and water quenching.

These experimental results show that the hardness of martensite is practically independent of the quenching temperature and of the cooling rate. It is not conceivable that the grain size is unaffected by these factors. Indeed the author indicates that the grain size is a function of both the quenching temperature and the cooling rate. Hence the hypothesis is not compatible with the observed hardness relations.

On the other hand, there is substantial evidence that the hardness is directly related to the amount of dissolved carbon. The amount

<sup>16</sup> Bureau of Standards Progress Report to the Gage Steel Committee, No. 12.

of dissolved carbon is not affected by the quenching temperature, when the critical ranges are exceeded, or by the cooling rate, when it is faster than the critical cooling rate. The effect of these variables on the hardness is also insignificant and indicates a close relation between the hardness and the amount of dissolved carbon. This conclusion is further supported by the observed relations between hardness and tempering temperature. It has been shown from the intensity of the

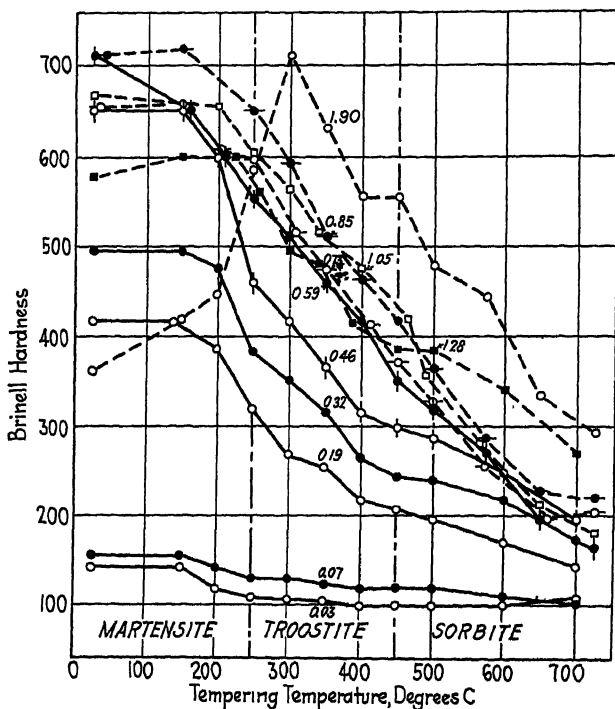


FIG 8.

heat evolution on reheating hardened carbon steels<sup>17</sup> that the amount of dissolved carbon decreases with increasing rate as the temperature is raised up to 260° C. The hardness varies in the same manner, Figs. 7 and 8. The inference is obvious; the hardness of martensite is directly associated with the amount of dissolved carbon. The author states that carbon distorts the space lattice of iron and has a strong chemical affinity for iron. Are not these facts sufficient to explain the great hardness of martensite without recourse to the involved grain size theory?

In developing his argument, the author states that freshly quenched martensite is in a transient condition. He implies that the changes with

<sup>17</sup> Bureau of Standards *Sci. Paper* 396.

time are caused by sluggishness of the hardening transformation and by the precipitation of carbon from solid solution. It can be shown that neither of these changes is of sufficient magnitude to justify this assertion without qualification. The first proposition, that the change from austenite to martensite is not complete when room temperature is reached, is contradicted by the length changes of hardened steel with time. Measurements of the changes with time of normally water-hardened steel untempered from the initial length measured a few hours after hardening show a consistent shrinkage. An austenitic carbon steel behaved in the same way. If the transformation continued with time the steel would expand.

That there is a precipitation of carbon with time is true; the shrinkage with time indicates that. The change is, however, very small and even in the most pronounced cases is less than 0.0005 in. per in. This shrinkage is less than that produced by tempering at 100° C. The heating curves of hardened steels, referred to above, show that the amount of carbon precipitated at so low a temperature as this is insignificant in comparison with the total amount dissolved. There is, then, no significant difference between martensite freshly quenched to ordinary temperatures and the same material after aging, at ordinary temperatures, for weeks, months, or years.

In conclusion, it should be stated that martensite is here used in the sense of a mixture of alpha- and gamma-iron solid solutions. There is considerable evidence, including that from x-ray analysis, that there is some austenite in normally hardened tool steel. If this term is restricted to the pure alpha-iron solid solution, as the author appropriately suggests, we lose a convenient term for the description of hardened tool steel and must substitute a cumbersome one such as martensite-austenite or else invent another.

EDGAR C. BAIN (author's reply to discussion).—The procedure, described by Mr. Rawdon, for hardening iron by rapidly quenching a small lake of the molten metal in a cold block by means of its own thermal conductivity is very interesting. Assuming that no contamination of the iron took place, one may well be surprised at the formation of carbonless martensite in this manner. Such a rapid quench from such a high temperature, however, might well produce very fine grains and purely crystallized grains as well. It would appear that no precautions were taken to preclude the formation of the nitride of iron from the air, and this nitride may well function similarly to cementite in the formation of a kind of martensite. Until these experiments are repeated in vacuo, and inert gases, they cannot be considered as demonstrating the hardening of pure iron.

Referring to Mr. Scott's discussion, it is generally accepted, as has been said, that the hardness of martensite of a definite carbon content is



not greatly affected by the quenching temperature, or cooling rate, provided that the cooling rate is more rapid than a certain critical one. This is to be expected, because if the cooling rate is sufficiently rapid to carry the steel below the normal transformation point as austenite, the martensite results after some time at 300° to 400° F. Martensite forms in carbon steels, apparently, in any event, only at this low temperature. If the carbon content is unusually high, the austenite persists even then. With very low carbon content, there is no characteristic formation of martensite at this temperature, and the grain refinement then depends on the rate of cooling through the range of gamma-alpha transformation. It is then, not incompatible with the argument to find that martensite hardness is largely unchanged with rate of cooling and temperature of quench.

## Stainless Steel, with Particular Reference to the Milder Varieties (Stainless Iron)

By JOHN H. G. MONYPENNY,\* F. INST. P., SHEFFIELD, ENGLAND

(New York Meeting, February, 1924)

THE range of chromium content of stainless steel is, in most cases, included in the limits 11 to 14 per cent., or the middle part of the range, 9 to 16 per cent., specified by the discoverer. For some time after the steel was produced commercially, the carbon content was about 0.3 to 0.4 per cent. and occasionally higher; only rarely was material with 0.25 per cent. carbon or less produced. The reason for this is obvious from the nature of the alloys of chromium available for making such steels; as the lowest carbon content generally available was about 1 per cent., and this in conjunction with a chromium content of about 60 per cent., the production of a 12-per cent. chromium steel with less than 0.25 to 0.30 per cent. carbon was impossible. The advent, on a reasonable commercial scale, of carbonless ferrochromium has modified this condition, however, so that for the last three years stainless material containing 0.1 per cent. or less carbon and the normal amount of chromium has been on the market. As far as the author is aware, the material was first made on a commercial scale by the firm with which he is associated in June, 1920, when a 5- or 6-ton cast of material containing 0.07 per cent. carbon and 11.7 per cent. chromium was made and cast into 12-in. ingots.

The necessity for using a totally different raw material, carbonless ferrochromium, instead of the ordinary low-carbon ferro (0.6 to 1.0 per cent. carbon) has led to the idea that stainless iron is a quite distinct product and quite different from stainless steel. While this may be true from a commercial aspect, it is wrong metallurgically. The name stainless iron is unfortunate as the material is a very mild stainless steel and forms the lowest carbon member of a series of steels of continuously varying content which are, in many respects, the counterpart of the series of ordinary carbon steels ranging from "dead soft" to tool steels. In an article on stainless steel in the *Journal* of the Society of Chemical Industry, November, 1920, the author said "Just as in the far-off days 'steel' was regarded as a hard product of iron, and little or no attempt was made to grade it into harder or softer varieties, so at present stainless

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steel is, to most people, a product having only one distinct set of properties, many regarding it solely as a special type of cutlery steel. In times gone by, as the use of steel became more general, it was realized that by varying the content of carbon or manganese, steels of widely different intrinsic hardness could be produced, and for each purpose some definite 'temper' of steel was best suited. In the same way, as the use of stainless steel becomes more general, it will be found that products of different intrinsic hardness (corresponding to the varieties of ordinary steel) can be produced, all of them having the distinguishing property of great resistance to corrosion, but varying among themselves as soft or mild steel differs from file steel. For each use of stainless steel there will be an optimum temper."

The addition of large amounts of chromium to steel produces a number of characteristic effects on the properties of the steel. Of these effects, the four following are of particular interest from the point of view of the general properties of stainless material. The addition of chromium to steel: (1) Lowers the carbon content of the eutectoid, pearlite, to a considerable degree; (2) raises the temperatures at which the carbon change points ( $Ac_1$  and  $Ar_1$ ) occur; (3) diminishes very markedly the speed of diffusion of the carbon in the steel; (4) induces notable air-hardening properties in the material.

In a previous paper<sup>1</sup> the author described a series of experiments for determining the eutectoid ratio of a series of chromium steels and also of the solubility lines of the excess carbide. From the results obtained, the value of the eutectoid composition, as affected by varying chromium content, was plotted in a curve, which is reproduced in Fig. 1. From this it will be seen that at 12 per cent. chromium the eutectoid contains slightly more than 0.3 per cent. carbon. Further work by the author using as a base the lower carbon material now available (and which he hopes to have ready for publication in the near future) has shown that these earlier determinations were substantially accurate. It will be evident from the value of the eutectoid in stainless material that carbon has a much greater effect in producing steel in such high-chromium material than in iron free from this alloying metal, and also that the range of carbon content of such high-chromium steels is much more restricted than in chromium-free steels. For example, from a structural point of view, annealed material containing 12 per cent. chromium and 0.5 per cent. carbon corresponds to a tool steel containing 1.3 to 1.5 per cent. carbon.

The changes in structure and properties induced in all stainless steels will be much more readily understandable if attention is first given to a steel of eutectoid composition, or very slightly hypoeutectoid. As a

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<sup>1</sup> The Structure of Some Chromium Steels. *Jnl. Iron and Steel Inst.* (1920) 101, 493.

convenient starting point, it is well to obtain the steel as a homogeneous mass of martensite and because chromium raises the temperature at which  $Ac_1$  occurs and diminishes the speed of diffusion of the carbide, a fairly high temperature is necessary to obtain this. If such a steel containing 12 per cent. chromium and 0.25 to 0.3 per cent. carbon is quenched or air cooled in reasonably small pieces from a temperature of  $1000^{\circ}\text{C}$ . or over, it will consist entirely of martensite and will have a Brinell hardness number of the order of 500. In this condition, the whole of the chromium is in solution in the iron. By tempering, changes are produced similar to those obtained on heating a hardened sample of ordinary carbon steel, except that the changes occur at much higher temperatures. With the stainless sample, the martensite remains almost unchanged up to about

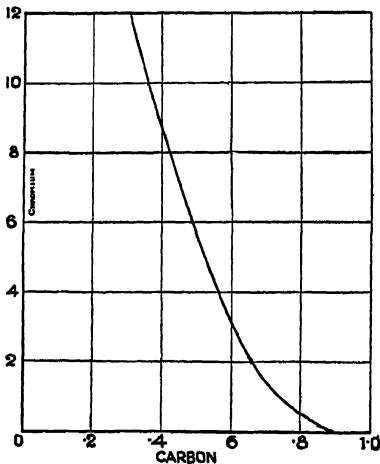


FIG. 1.—INFLUENCE OF CHROMIUM ON EUTECTOID POINT OF STEEL.

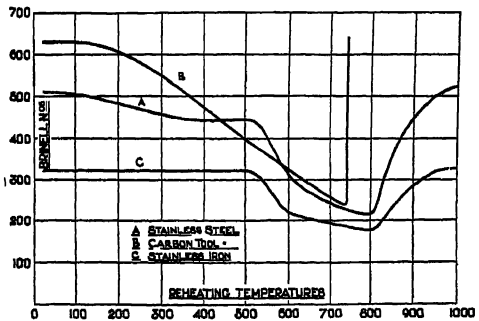
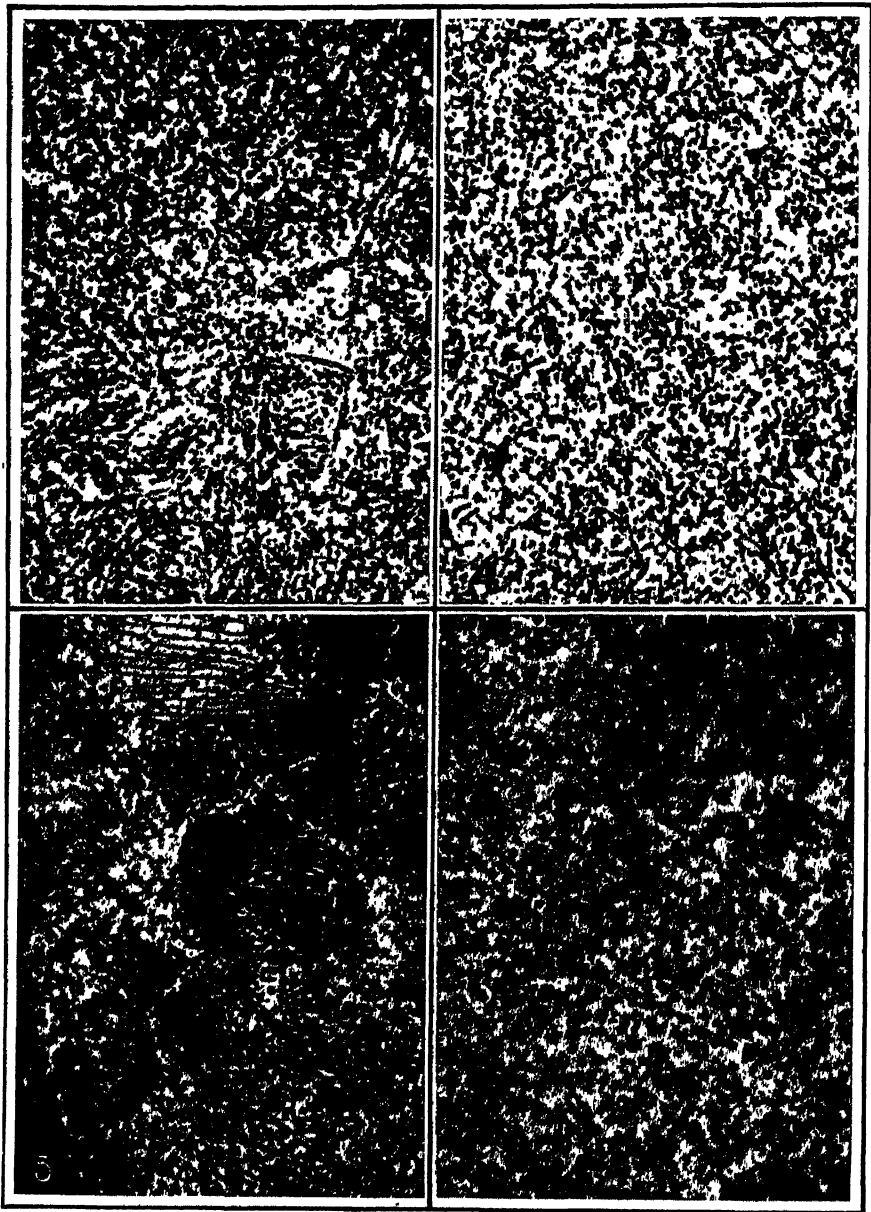


FIG. 2.—INFLUENCE OF TEMPERING ON THE BRINELL HARDNESS OF PREVIOUSLY HARDENED SAMPLES (ALL PIECES WATER-QUENCHED FROM TEMPERING TEMPERATURES). CURVE A, STAINLESS STEEL OF EUTECTOID COMPOSITION HARDENED AT  $1050^{\circ}\text{C}$ . CURVE B, ORDINARY CARBON TOOL STEEL. CURVE C, STAINLESS IRON HARDENED AT  $950^{\circ}\text{C}$ .

$500^{\circ}\text{C}$ . the hardness being also almost unaffected. Between  $500^{\circ}$  and  $600^{\circ}\text{C}$ ., tempering takes place rather suddenly and the hardness falls rapidly to about 250 to 300. The martensite, meanwhile, is replaced by very fine sorbite or troostite, consisting of very fine particles of carbide, almost ultramicroscopic, embedded in a ground mass of ferrite. From  $600^{\circ}\text{C}$ . up to about  $750^{\circ}$  to  $800^{\circ}\text{C}$ ., the hardness falls slowly and steadily to about 200 and in this range the particles of carbide, which have separated out previously, gradually coalesce into larger globules. Curve A, Fig. 2, shows the Brinell hardness numbers obtained on tempering such a steel at gradually increasing temperatures. Curve B represents the results obtained on ordinary carbon tool steel. The three ranges of temperature described above are clearly indicated in curve A; on the other



FIGS. 3-6.—MICROSTRUCTURE OF STAINLESS STEEL 0.3 PER CENT. CARBON (APPROXIMATELY EUTECTOID).

FIG. 3.—HARDENED AND TEMPERED 750° C.  $\times 1000$ .

FIG. 4.—HARDENED 900° C.  $\times 1000$ .

FIG. 5.—ANNEALED AT 1050° C. (PEARLITIC).  $\times 1000$ .

FIG. 6.—ANNEALED AT 900° C. (GLOBULAR).  $\times 1000$ .

hand the hardness of the tool steel falls almost uniformly. On continuing the heating of the stainless steel, the  $A_{c1}$  change occurs at about  $800^{\circ}\text{C}$ . or higher, there being a well-defined absorption of heat. Whereas in ordinary steels, the solution of the carbide at the  $A_{c1}$  point takes place very rapidly, in stainless steels, as in all high-chromium steels, it takes place much more slowly. The consequence is that in such steels the absorption of heat, which is generally referred to as  $A_{c1}$ , is only the commencement of that change for only part of the eutectoid carbide dissolves, the remainder going progressively into solution as the temperature rises over a range of  $150^{\circ}$  to  $200^{\circ}\text{C}$ . (For convenience, however, this point will hereafter be referred to as  $A_{c1}$ .) As a result, stainless steel does not attain its full hardness on quenching immediately above the  $A_{c1}$  point; the hardness increases as the temperature rises over the range mentioned above, as shown in the right-hand portion of curve A, Fig. 2. Fig. 3 shows the structure of stainless steel containing 0.3 per cent. carbon after hardening and fully tempering while Fig. 4 shows the same steel hardened at  $900^{\circ}\text{C}$ . and illustrates the amount of carbide still undissolved. When quenched from  $1000^{\circ}\text{C}$ . or over, the structure of such a steel consists of martensite only.

The effect of chromium in retarding the solution of the eutectoid carbide is evident even with small amounts of chromium; thus, in the paper previously mentioned, the author showed that a steel with 0.37 per cent. carbon and 2.8 per cent. chromium (the eutectoid for this amount of chromium contains 0.62 per cent. carbon) contained quite a large amount of free carbide when quenched from  $850^{\circ}$  after soaking at that temperature 1 hr., notwithstanding the fact that the  $A_{c1}$  point occurred about  $60^{\circ}\text{C}$ . lower, or at  $790^{\circ}\text{C}$ . More recently, Whiteley<sup>2</sup> has shown that there is a similar lag, though over a very much smaller range of temperature, in the solution of part of the carbide of the pearlite in ordinary carbon steels.

It has been mentioned that high-chromium steels possess notable air-hardening properties. The production of hardness, however, depends on the rate of cooling in precisely the same way as with ordinary carbon steels, although the actual values of the rates necessary to give similar effects with the two types of steel are widely different. Thus with ordinary carbon steel, recent experiments by Portevin and Garvin<sup>3</sup> have shown that to harden such steel the rate of cooling should be such that the time taken to cool from  $700^{\circ}$  to  $200^{\circ}\text{C}$ . is not more than about 10 sec. With stainless steel, however, much slower rates may be used and the steel remain hard. There is, nevertheless, a fairly definite rate of cooling that must be exceeded to bring about hardening; the rate, however, varies, in any given steel, with the temperature from which the steel is

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<sup>2</sup> *Jnl. Iron and Steel Inst.* (1922) 105, 339.

<sup>3</sup> *Jnl. Iron and Steel Inst.* (1919) 99, 469.

cooled. The higher this temperature is above the  $A_{c1}$  point, the slower is the rate at which the steel may be cooled and yet be hardened. This is illustrated in Fig. 7, which represents the Brinell hardness numbers obtained on samples of stainless steel of approximately eutectoid composition

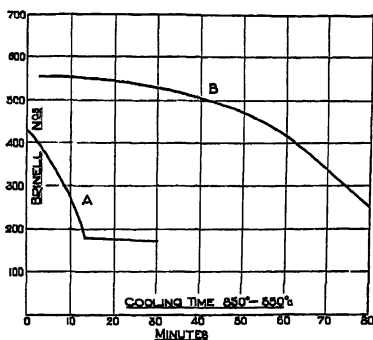


FIG. 7.—INFLUENCE OF COOLING RATE ON BRINELL HARDNESS OF STAINLESS STEEL. CURVE A, COOLED FROM 860° C. CURVE B, COOLED FROM 1200° C.

position cooled at different rates from 860° and from 1200° C., the rate of cooling being measured by the time taken to cool over the range 850° to 550° C. To obtain a Brinell hardness number of at least 400, the cooling time should not exceed about 2 min. when cooled from 860° but may reach 60 min. when the maximum temperature is 1200° C. With slower rates of cooling than these, the steels become progressively softer until the completely annealed condition is obtained. If the maximum temperature has been sufficiently high to dissolve all the carbide, on complete annealing, a pearlitic structure is obtained as shown in Fig. 5. If, however, the whole of the carbide was not dissolved, the structure is granular (Fig. 6), being similar to that produced on hardening and fully tempering, except that the granules of carbide are much coarser. In either case the steel has a tensile strength of about 40 tons per square inch and is properly described as being in the annealed condition. It will be obvious from what has been said and from Fig. 7 that if it is necessary to anneal the steel for any particular purpose, the temperature of annealing should exceed the  $A_{c1}$  point by as small a margin as possible in order that the cooling period may not be unduly prolonged in obtaining the maximum softness.

When annealed at high temperatures (*i.e.*, 950° C. and above), lower carbon steels show mixtures of ferrite and pearlite similar to those of ordinary mild steels, except that there is a distinct tendency for the ferrite to contain isolated globules and laminae of carbide. Fig. 8 shows an annealed steel containing 0.15 per cent. carbon. When the carbon is reduced to the limits generally found in stainless iron, the carbide in the pearlite tends to ball up so that such low-carbon material, when annealed, often consists of ferrite grains with globules of carbide (see Fig. 9). On the other hand, when air cooled or quenched from such high temperatures, these hypoeutectoid steels consist entirely of martensite, unless the carbon content is very low, when free ferrite may also be present, depending on the rate of cooling and on the composition of the steel (apart from carbon and chromium).

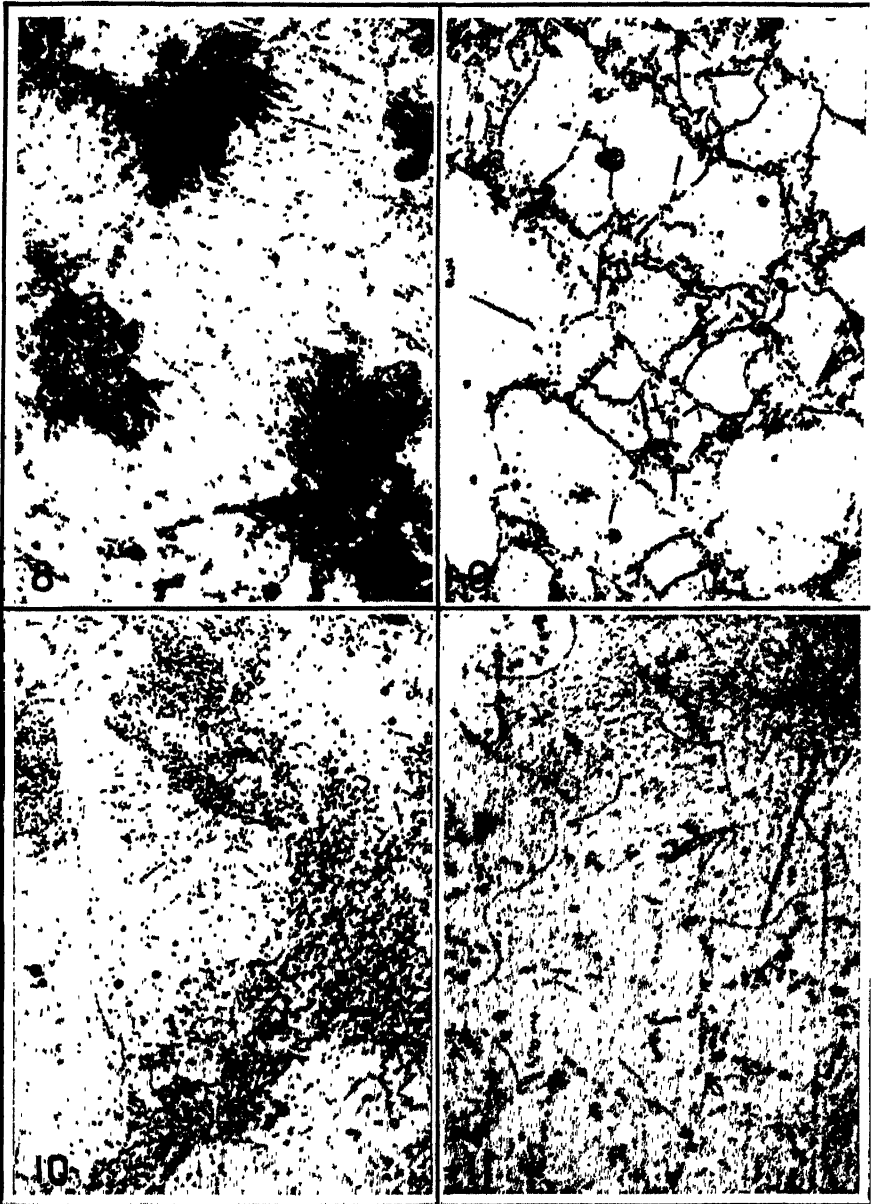


FIG. 8.—MILD STAINLESS STEEL 0.15 PER CENT. C, ANNEALED 1050° C.  $\times 750$ .

FIG. 9.—STAINLESS IRON 0.07 PER CENT. C, ANNEALED 1050° C.  $\times 750$ .

FIG. 10.—MATERIAL IN FIG. 8 AFTER WATER HARDENING AT 900° C. (SHOWING CARBIDE UNDISSOLVED).  $\times 750$ .

FIG. 11.—STAINLESS IRON 0.07 PER CENT. C AND 13.3 PER CENT. Cr, WATER QUENCHED 875° C. SHOWING CARBIDE UNDISSOLVED.  $\times 1500$ .



On tempering hardened samples of the low-carbon alloys, the Brinell hardness number falls in a manner analogous to that of the higher carbon steel, as shown in curve *C*, Fig. 2. On passing the carbon change point, the carbide in the pearlite behaves in a similar manner to that in eutectoid steel; that is, part of it dissolves at the actual absorption of heat and the remainder as the temperature rises. The temperature required for complete solution of the carbide under ordinary conditions of heating (*e.g.*, soaking for  $\frac{1}{2}$  to 1 hr. at maximum temperature) depends on the previous distribution of the carbide; if the latter is evenly distributed, as occurs when a previously fully hardened sample is reheated, the complete solution is obtained somewhat earlier than if the steel were previously annealed so as to give a structure of ferrite and pearlite. The persistence of the carbide particles may be illustrated by Fig. 10, which shows the steel in Fig. 8 after heating for 1 hr. at 900° C. followed by quenching in water. Even in extremely mild steels, carbide may be detected in samples quenched 50° to 100° above the carbon change point; Fig. 11 shows a steel with 0.07 per cent. carbon and 13.3 per cent. chromium water-quenched at 875° C. and shows the presence of ferrite, martensite and free carbide.

The  $A_{c3}$  line for these steels has not been completely worked out—its position appears to vary with variations in content of silicon, manganese, and nickel, small but varying amounts of which are almost invariably found in stainless steel. The ferrite however is gradually dissolved as the temperature rises above the  $A_{c1}$  point; Figs. 12 and 13 show the steel mentioned above (carbon 0.07 per cent. and chromium 13.3 per cent.) after quenching from 850° and 900° C., respectively. At higher temperatures the structure became entirely martensitic. After hardening and tempering, the low-carbon alloys consist of ferrite with globules of carbide evenly distributed (see Fig. 14).

Hypereutectoid steels behave in a manner analogous to ordinary high-carbon steels. The excess carbide gradually dissolves after the pearlite carbide has been completely taken into solution. In the paper previously referred to, the author traced out the solubility line of the free carbide in a steel containing 11.2 per cent. chromium.

#### INFLUENCE OF COMPOSITION AND HEAT TREATMENT ON RESISTANCE TO CORROSION

Whatever theory is held as to the cause of the corrosion of iron, there can be no doubt that commercially pure iron is soluble in water of ordinary purity. By the presence of sufficient chromium in solid solution in the iron, this solubility is reduced practically to zero. There is also little doubt that heterogeneity in a metal tends to increase corrosion owing to galvanic effects. This is noticeable in the case of ordinary steels;

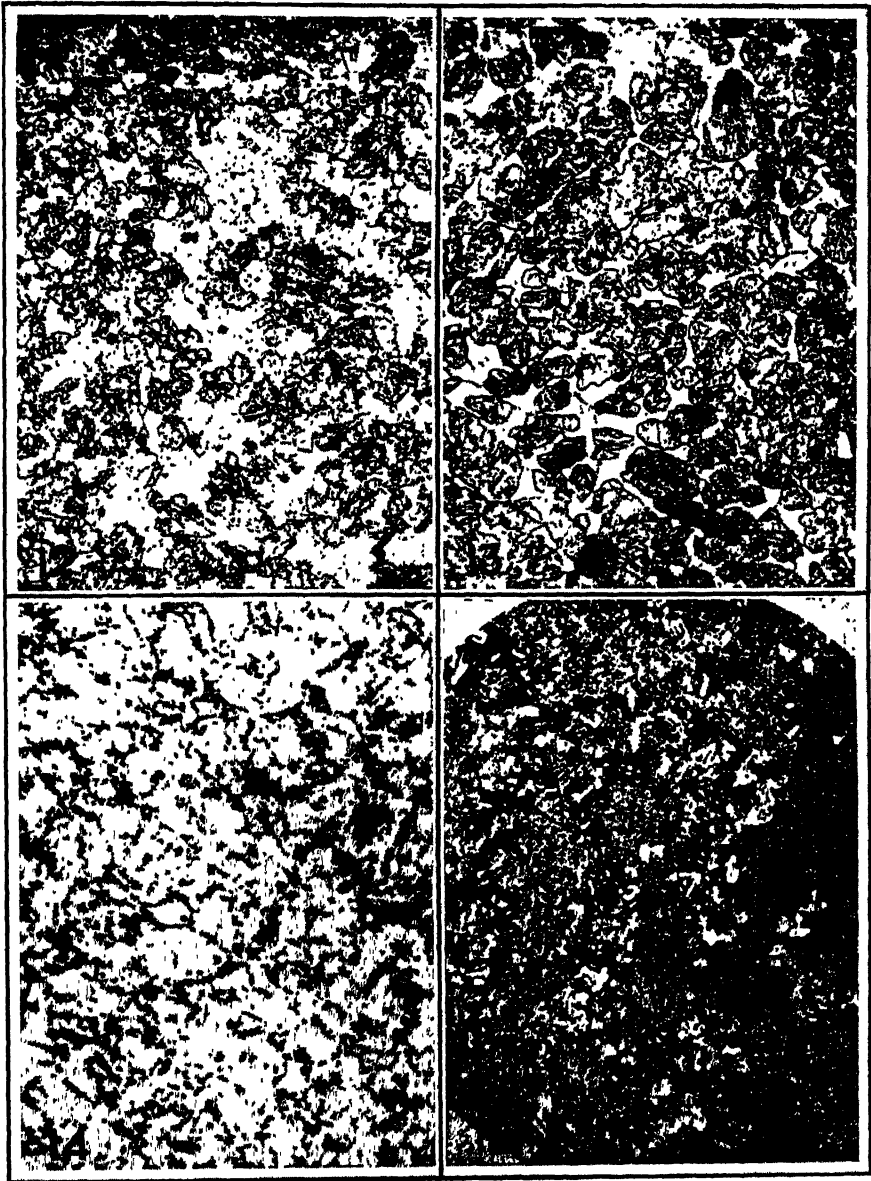


FIG. 12.—STAINLESS IRON 0.07 PER CENT. C, 13.3 PER CENT. Cr, WATER HARDENED 850° C. (BRINELL 238).  $\times 750$ .

FIG. 13.—STAINLESS IRON 0.07 PER CENT. C, 13.3 PER CENT. Cr, WATER HARDENED 900° C. (BRINELL 281).  $\times 750$ .

FIG. 14.—STAINLESS IRON 0.07 PER CENT. C, 13.3 PER CENT. Cr, HARDENED 950° C. AND TEMPERED 700° C. (BRINELL 174).  $\times 1000$ .

FIG. 15.—HIGH-CARBON STAINLESS STEEL (1.0 PER CENT. CARBON) SHOWING CORROSION ROUND CARBIDE.  $\times 500$ .

the carbide present is electronegative to the iron and, other things being equal, steels tend to corrode faster than pure iron. The same effect is obtained in stainless steels; with any given steel, the greatest resistance to corrosion is obtained after quenching in such a manner as to give a homogeneous martensite while the least resistant form produced by heat treatment is obtained by annealing the steel so as to produce a complete separation of carbide and ferrite.

In the case of stainless steels, the separation of carbide not only tends to decrease the resistance to corrosion, owing to galvanic effects, but it lowers the concentration of the chromium in solution in the iron, for the carbide that separates out contains a large amount of chromium; hence the ground mass of iron is not so insoluble as when it contained the whole of the chromium in solution. The actual composition of the carbide in stainless steel has not been settled definitely but the ratio of chromium to carbon in it is approximately 10 to 1. The presence of about 0.3 per cent. carbon, therefore, locks up about 3 per cent. chromium in the carbide and hence reduces by that amount, in a fully annealed steel, the chromium available for conferring insolubility.

With any given steel the effect of variations in heat treatment may be summarized as follows:

### *Hardening*

The greatest resistance will be obtained by quenching from a temperature sufficiently high to dissolve all the carbide in the steel. In practice, however, it is found that with a temperature of 900° to 950° C., the ground mass produced on quenching a steel of normal composition is practically insoluble in water and that increasing the temperature beyond this range produces no marked improvement; on the other hand it seriously increases the risk of cracking during hardening.

### *Tempering*

From the fact that no appreciable loss in hardness is obtained by tempering up to 500° C. and also that after such tempering the structure of a previously hardened sample is still martensitic, it would not be expected that such tempering would have any great effect on the resistance to corrosion of the hardened material. This has been found, experimentally, to be the case and it is of great importance commercially, for such tempering removes, to a great extent, the internal stresses set up during hardening and also improves the ductility of the steel.

The sudden marked fall in hardness produced on tempering between 500° and 600° C. is accompanied by a lessened resistance to corrosion of

the material. Such material may stain when tested with vinegar<sup>4</sup> (depending on the carbon and chromium contents) but even on prolonged immersion in this fluid it is attacked extremely slowly. It is practically insoluble in water; for example, small cylinders of the steel in this condition have been kept in slowly running water for over 12 months without the slightest signs of any action taking place. Similar samples kept on the seashore between high- and low-water marks for 6 months have shown only quite negligible amounts of corrosion.

Very little effect is produced by increasing the tempering temperature from 600° C. up to about 750° C. Much of the tempering effect taking place in this range of temperature is due to the coalescence into larger globules of the carbide previously separated.

### *Annealing*

It has already been mentioned that stainless material is less resistant when annealed than after other forms of heat treatment. Even when annealed, however, it rusts extremely slowly.

### *Cold Work*

Although possibly not strictly a condition of heat treatment, it may be convenient to consider the effects of cold work on the resistance of stainless material. Most metals distorted by cold work have a greater tendency to corrode than when in the normal condition. Stainless steel is no exception to this and when severely distorted it rusts comparatively readily; for example, a coil of severely cold-drawn wire will rust into a solid mass if left exposed to the atmosphere for a few months. The comparative resistance of the distorted and undistorted material can be shown by placing half a broken tensile test piece of stainless steel, hardened and tempered (which had been polished all over before breaking) in a solution of sodium chloride; corrosion will commence at the distorted end. As to whether corrosion will take place or not under stated conditions, after a small amount of distortion, depends on the composition of the steel and can only be settled by actual experiment but the lessened resistance is always produced just as it is by tempering a hardened sample. It is for this reason that a polished surface on stainless steel is more resistant than a roughly machined surface; the effect is due, however, not to the presence of polish on the former but to the absence of the distorted skin which is produced by rough machining. There is also an indirect advantage in a polished surface; such a surface, being

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<sup>4</sup> The vinegar test consists in placing a drop of vinegar on a polished surface and allowing it to dry; this test is more severe than placing the article in vinegar for 12 to 24 hours.

smooth, offers less opportunity for the lodgment of dust than a rough surface and, therefore, less chance of local pitting because of galvanic effects liable to be produced by some kinds of dust.

### *Composition*

The important variables from the point of view of corrosion are the chromium and carbon contents. Normal stainless steel contains 11 to 14 per cent. chromium; with less than 11 per cent. chromium, a notable resistance to corrosion may be obtained if the carbon content and heat treatment are suitably chosen. For example, steel containing 8.6 per cent. chromium, after it had been water-quenched from 1150° C., was quite stainless to vinegar but its mechanical properties in this condition were an effective bar to its use for many purposes.

In a similar manner, increasing the chromium content to 20 or 30 per cent. increases the resistance to general corrosion and minimizes the effects of heterogeneity due, for example, to high carbon content. Such alloys, however, cannot, in general, be hardened and their mechanical properties are not suitable in many cases. For similar reasons and as the cost of the higher chromium alloys is great, the amount of chromium usually found in stainless material lies between 11 and 14 per cent. Steels in this range containing less than about 0.4 per cent. carbon are stainless to vinegar when suitably hardened.

As the carbide in stainless steel contains a large amount of chromium and as for many engineering purposes the steel must be in a condition in which the carbide is mainly out of solution in order that the material may have suitable mechanical properties, from the point of view of non-corrosive properties, the less carbide there is the better. The amount of carbon, however, is generally governed, to a great extent, by the mechanical properties desired in the material. When large amounts of carbon are present, all the carbide is not dissolved even when heated to 1200° C. and quenched. Such a high-carbon steel corrodes at a much greater rate than one of lower carbon content, the corrosion commencing around the carbide particles; this is shown in Fig. 15, where the dark areas around the white carbide represent the corroded parts. The sample contained 1.0 per cent. carbon and had been tested with vinegar.

### *Scale*

Although not exactly a variable in composition, it may not be out of place to consider here the action of scale. Stainless material heated to temperatures above a red heat, whether followed or not by rolling or forging, is coated with scale, consisting of the oxides of iron and chromium. The scale is electronegative to the metal and, if not removed, will cause

local corrosion in its neighborhood. Articles made of stainless material that will not be machined or ground all over should, therefore, have the scale completely removed by pickling. Sand blasting does not appear to be so effective in removing all the scale; there is a tendency for particles of it to be forced into the metal by the blast.

### PROPERTIES OF STAINLESS IRON

Dealing briefly with its manufacture, stainless iron is produced in the basic-lined electric furnace. Before adding the chromium alloys, the carbon content of the bath should be reduced well below 0.10 per cent. and afterwards precautions taken to avoid contamination with carbon, which is greedily absorbed by the molten material. Because of its greater softness, stainless iron forges more easily than the harder varieties of stainless material; it works probably as easily as ordinary steel containing about 0.4 per cent. carbon and hence may readily be forged, rolled, or drop stamped.

Stainless iron does not air harden so intensively as the higher carbon varieties. It does air harden but the degree of hardness produced is considerably less, being generally in the range 280 to 380 Brinell instead of 450 to 550 as obtained with a steel containing 0.3 per cent. carbon. Hence it is much safer to work and heat treat than the higher carbon varieties; it is much less liable to develop hardening cracks so that, in general, it may be air cooled after forging without danger. Reasonable care, however, should be taken; for example, forgings should not be thrown on a wet floor or in a drafty place. Should any trouble arise, owing for example to intricate shapes in drop stamping, all danger of cracking may be removed by recharging the hot forgings into a furnace maintained at 650° to 700° C. and allowing them to soak for about 1 hr. after they have attained the furnace temperature. By so doing the carbon change takes place and the forgings, being then in the annealed condition, may be withdrawn from the furnace and air cooled without danger.

The suitability of any material for engineering purposes is judged, to a large extent, by its mechanical properties and the type of the latter desired depends on the purpose to which the material is to be applied. The results obtainable from stainless iron after oil hardening and then tempering at varying temperatures are typified in Figs. 16 and 17, which show the results on material containing respectively 0.07 and 0.10 per cent. carbon; the former hardened to approximately 73 tons tensile strength and the latter to 85 tons. Both were heated in the form of bars  $1\frac{3}{8}$  in. in diameter but results of the same order would be obtained with bars of considerably larger size. The tensile test pieces were the British standard size (2 by 0.564 in. diameter). The impact tests were

obtained with an Izod machine, the test pieces being of standard size (10 mm. square) and having the standard V notch. The tests in Fig. 16 were obtained on the first cast of stainless iron produced commercially. For such steels, a temperature of 950° C. is recommended for hardening. It is sufficiently high with material of normal composition to insure solution of the ferrite and carbide and thus give a homogeneous martensite on quenching.

The fall in tensile strength produced by tempering at successively higher temperatures is what would be expected from the Brinell hardness results given earlier. Up to a temperature of 500° C., there is little or no reduction in tensile strength while the test piece shows increased ductility due, at any rate in part, to the relief of stresses set up during hardening. Between 500° and 600° C. the hardness falls quickly, while from 600° to about 750° C. it falls slowly and steadily. The very slow rate of fall in tensile strength with increase of tempering temperature in the range 600° to 750° C. is very useful, commercially, as it permits quite a wide range of temperature to be used when a number of articles have to be tempered to produce a given tensile strength, obviously a desirable thing. On the other hand, the comparatively rapid fall of hardness in the range 500° to 600° C. makes the difficulties of tempering in this range correspondingly great.

In the annealed condition, the material has a somewhat lower tensile strength than after hardening and tempering and a much lower yield point, as will be seen from the following tests of two typical casts:

YIELD POINT, TONS PER SQUARE INCH	MAXIMUM STRESS, TONS PER SQUARE INCH	ELONGATION, PER CENT.	REDUCTION OF AREA, PER CENT.	IZOD IMPACT, FOOT-POUNDS
20.2	34.1	39.0	72.0	92
20.8	35.2	35.0	66.8	68, 60

Comparing these with values plotted in Figs. 16 and 17 shows that they bear the same relation to the latter that a normalized test on an ordinary mild steel does to a hardened and tempered test on the same steel.

Tests at temperatures above atmospheric show that in the range of temperature likely to be met with in the use of superheated steam stainless iron retains its tensile strength very well. This is illustrated by the curves in Fig. 18, which shows the tensile results obtained on a sample of stainless iron containing 0.07 per cent. carbon and also on mild stainless steel containing 0.16 per cent. carbon, at the temperatures indicated. The test pieces were machined to 2 by 0.564 in. parallel and the pulling speed was  $\frac{1}{16}$  in. per minute.

Stainless iron may be readily cold worked and, provided the amount of distortion produced is not unduly great, the resistance to corrosion is not seriously affected. It has been successfully drawn into wire and tubes

and, although more difficult to draw than ordinary mild steel, is considerably better in this respect than the higher carbon varieties of stainless

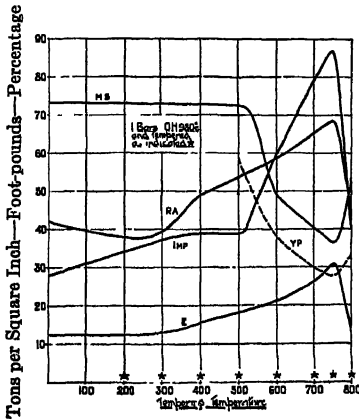


FIG. 16.—MECHANICAL PROPERTIES OF STAINLESS IRON 0.07 PER CENT. C, 11.7 PER CENT. Cr, 0.08 PER CENT. Si, 0.57 PER CENT. Ni, 0.12 PER CENT. Mn.

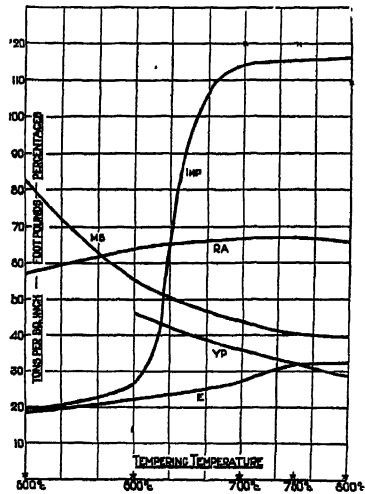


FIG. 17.—MECHANICAL PROPERTIES OF STAINLESS IRON 0.10 PER CENT. C, 11.5 PER CENT. Cr; BARS  $1\frac{1}{8}$  IN. DIAMETER, OIL HARDENED AT 950° C., AND TEMPERED AS INDICATED BY \*.

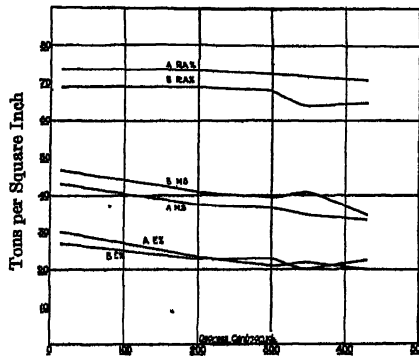


FIG. 18.—TENSILE TESTS AT TEMPERATURES ABOVE ATMOSPHERIC ON STAINLESS IRON AND MILD STAINLESS STEEL. A, STAINLESS IRON 0.07 PER CENT. C, 0.27 PER CENT. Si, 0.17 PER CENT. Mn, 11.9 PER CENT. Cr, 0.28 PER CENT. Ni; B, MILD STAINLESS STEEL 0.16 PER CENT. C, 0.52 PER CENT. Si, 0.27 PER CENT. Mn, 13.0 PER CENT. Cr, 0.31 PER CENT. Ni.

NOTE.—In Figs. 16, 17, and 18, the ordinates for maximum stress (M.S.) and yield point (Y.P.) are tons per square inch (1 ton = 2240 lb.); the values for impact are given in foot-pounds.

material. Probably a great part of the difficulty consists in the fact that stainless iron does not flow in the same way as mild steel and hence



cannot be treated in the same fashion. The procedure during drawing must be modified somewhat. Stainless iron may be cold pressed into a variety of forms with considerable ease. Its hardness and tensile strength are, of course, greater than that of some metals extensively used for sheet work, *e.g.* German silver and aluminum, hence it requires heavier pressure. If the sheet is distorted, during the pressing operation, to such an extent as to affect seriously its rust-resisting properties, the latter may be fully restored by air hardening and tempering. If this treatment is carried out when the greater part of the cold-working operation has been performed and the article subsequently pickled to remove scale, the piece can be given the final pressing which will brighten up the dull pickled surface and thus materially assist any final polishing operation. This method may obviously be applied in other cold-working operations, *e.g.* bright drawn wire, cold-rolled strip, and the like. The small amount of distortion produced by the final cold-working operation will have a negligible effect on the resistance to corrosion.

For general engineering work, where material of about 40 tons tensile strength is required, there is little doubt that stainless iron is the most suitable form of stainless material to use. It drop stamps quite readily and is easily machined. It has been used for such widely diverse purposes as turbine blades, golf clubs, spoons and forks, bonnets and other fittings for motor cars, ornamental firegrates, spurs and many other articles. Because of its low carbon content, its resistance to corrosion is affected less by varying heat treatment than the higher carbon varieties. Thus, in its fully softened condition, it is stainless to the vinegar test even when the chromium is lower than is customary in stainless material, *e.g.* 10 to 11 per cent.

The general character of the resistance of stainless iron to various corroding media is similar to that of stainless steel except that, as stated earlier, it possesses these properties (under similar conditions of treatment, etc.) to an enhanced degree owing to the smaller amount of chromium locked up in the carbide. The author treated this part of the subject in some detail in a paper<sup>\*</sup> contributed to the general discussion on "Alloys Resistant to Corrosion" held by the Faraday Society in conjunction with other societies at Sheffield on April 13, 1923. Speaking generally, however, stainless material is resistant to water (tap, river, well, or sea water), vinegar, fruit and meat juices, ammonia, solutions of alkalis, alkaline carbonates, and many other aqueous solutions of salts. It is practically unaffected by strong nitric acid or nitric acid of specific gravity 1.20 (the strength that attacks ordinary steel most readily); it is, however, very slowly attacked by dilute nitric acid of about normal strength. It

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<sup>\*</sup> The Resistance to Corrosion of Stainless Steel and Iron. *Trans. Faraday Soc.* (1923) 19, pt. 2.

is attacked readily by hydrochloric, sulfuric and sulfurous acids. It is practically unaffected by saturated or superheated steam, lubricating oils, petrol, benzol, paraffin, greases, etc.; it has therefore a very considerable future before it in engineering work, particularly with regard to hydraulic and steam service work.<sup>6</sup>

The results of atmospheric corrosion depend on the location of the test. In towns, especially in the neighborhood of works, the atmosphere contains distinct amounts of acid and large amounts of dust, often ferruginous. Samples exposed for prolonged periods to such conditions become coated with a dark-brown coating, which however may often be rubbed or washed off leaving an almost unimpaired surface; at other times the coating appears to induce minute pits in the surface of the steel underneath, probably owing to the presence of small amounts of acid (sulfuric). In purer atmospheres (in country districts) stainless material will remain unattacked for long periods.

An important property of stainless material is that it resists oxidation remarkably well on heating to temperatures up to about 800° or 825° C., even for prolonged periods. At temperatures up to about 700° or 750° C., a series of temper colors are produced similar to those obtained on ordinary carbon steel but at much higher temperatures than with the latter material. Above 700° or 750° C. up to about 825° C., a polished surface of stainless steel or iron becomes covered with a gray film, without however losing its polished appearance and the specimen neither gains nor loses weight appreciably. Above 825° C., stainless steel or iron begins to scale appreciably.

In conclusion the author wishes to thank the Directors of Messrs. Brown Bayley's Steel Works for permission to publish the data contained in this paper.

## DISCUSSION

P. A. E. ARMSTRONG,\* Watervliet, N. Y. (written discussion).—This paper correctly places carbon in alloys of chromium, iron, and carbon. Earlier investigators, particularly Monnartz and Borchers, showed that carbon was an unimportant detail in high-chromium and iron alloys. Later, the work of Brearley and Haynes incorrectly taught us that carbon, chromium, and iron were important as alloys and had to be combined in certain definite percentages to produce rust-resisting steels; further, it was necessary to harden and polish.

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<sup>6</sup> For a general account of some experiences in this direction see: *Stainless Steel—Its Properties and Some of Its Engineering Applications*. *Proc. Cleveland Inst. of Eng.* (England) (March, 1923).

\* Vice-president Ludlum Steel Co.

Monnartz and Borchers prefaced their published work, of about 1910-1911, with a statement that the field of chromium and iron had been thoroughly investigated and each and everyone had a different story to tell. The reason that can be gathered from Monnartz' work, and by a close scrutiny of the prior investigators, is that each investigator tested this alloy from a different point of view. One used sulfuric acid, another nitric acid, etc. Naturally one investigator would report that the material corroded and another that it did not. As a matter of fact, there is little difference between results of any of the investigators and the total investigation throws excellent light on the properties of these alloys, including their rust-resisting properties. Monnartz exposed 14 per cent. and upwards chromium-iron alloys for over two years without producing rust. These results should not be read as affirmatives and negatives but merely for just what they portray as far as each investigator is concerned.

The author shows that chromium and iron are the controlling factors of the corrodibility of an alloy of this analysis and that carbon only increases the physical properties. Furthermore, carbon works against the non-corroding property, therefore is a detriment. If carbon is used, unless very high, it should be used in the alloy in the least harmful way; that is, the carbides that are, in some measure, responsible for corrosion should be dissolved in the iron and the only way to do this when the iron is in a solid state is by heat treatment. The higher the temperature to which the alloy is heated and the greater the rapidity with which it is cooled, the more the carbides will be in solution and in the least harmful form. Chrome carbides are very resistant to acid corrosion, therefore if carbon is to be used, the best results are obtained with very high carbon, 6 per cent. or higher, such as is found in high-carbon ferrochromium, not the low or medium carbons of Brearley and Haynes.

The author says that his company was the first to make a high-chromium iron on a commercial scale, having made it in 1920. Our company made such a material prior to 1920, also the work of early investigators was carried on many years prior to 1920; I believe the samples that were prepared at that time, during these investigations, were closely related to the product that was commercially available. The author thinks that the only reason why low-carbon high-chromium irons are now available is because the necessary ferrochromium can now be obtained. As a matter of fact it was obtainable many years prior to 1920; in fact, was a standard grade of ferrochromium.

A fact not generally known, brought out by the author, is the hardening by heat treatment of high-chromium and iron alloys containing practically no carbon. The low-carbon percentage he talks about is 0.07; he finds that by heating this chromium-iron alloy to a fairly high temperature and quenching, it becomes hard, 380 Brinell. My experience with alloys of this class shows this to be true; and a similar result can

be obtained with carbon lower than 0.07 per cent. I have tested alloys containing higher percentages of chromium than the ones the author mentions with carbon as low as 0.03 per cent. and a similar type of hardening is produced by quenching—350 to 380 Brinell seems to be about the figure. The same chromium-iron alloy slowly cooled, or so-called annealed, has a Brinell hardness of about 160. The point to consider now is what caused the hardening. It cannot be the carbon. This statement may create some surprise as we have always associated hardness by heat treatment as a direct result of carbon. The textbooks tell us that iron and chromium alloyed together cannot be made hard by heat treatment, in fact chromium alone will not harden iron. This oft-repeated statement is incorrect. Chromium and iron without any other alloying element will harden when subjected to heat treatment by being raised to a high temperature and quenched.

I believe that chromium and iron alloyed together and slowly cooled separate out into various constituents, one of which is pure iron; and when heated to a high temperature the iron is dissolved into the iron and chromium or the iron and chromium are dissolved into the iron and a greater resistance to deformation is obtained when the specimen is quenched. Therefore the Brinell test gives us a figure that is equivalent to hardness. Furthermore, the elastic limit has materially increased, likewise the ultimate strength, reduction of area and elongation have been correspondingly reduced. Under the microscope, a high-chromium iron with a small amount of carbon present, say less than 0.10 per cent., contains practically as many carbides after it has been quenched from a high temperature as it did when annealed, therefore the hardness cannot be the result of carbides being passed into solution by heat treatment but must have been due to some chromium and iron effect, perhaps a change in solid solution.

If other alloys are combined with chromium and iron, such as nickel, it is easier to hold the chromium in solid solution. Therefore heating to high temperatures and quenching produces a structure that is known as austenite and is comparatively soft; hardness is only brought about by drawing.

It has been contended that the alloy chromium, iron, and carbon is different from the alloy chromium, nickel, iron, and carbon because in one case quenching from high temperature makes hard whereas in the other quenching from high temperature makes soft; subsequent drawing makes the chrome-nickel alloy hard and subsequent drawing makes the other alloy soft. Obviously the difference is merely a form of solid solution well explained under the terms of austenite, martensite, sorbite.

It is essential that a better solvent than nickel should be employed so that the troublesome martensite is not readily formed. In other words,

what is necessary in a rustless iron should be true iron conditions of non-hardening. These can only be produced by a solvent that carries chromium and iron in solid solution all the time and is its normal structure. Silicon seems to be an excellent alloy for this purpose; 1 per cent. of silicon or thereabouts seems to be all that is necessary with high chromiums of 11, 12, or even higher percentages of chromium. Such an alloy will not harden when quenched from high temperatures if the carbon is low. Nickel additions to chromium are very susceptible to carbon influences. Whether the carbide is more easily dissolved or not, I do not know; but from microscopical observation I believe that to be the cause. The carbide is of a different chemical combination and more readily dissolves; so that with chromium and nickel it is essential to keep the carbon quite low if a highly ductile alloy is to be obtained and a minimum amount of hardness produced on cooling. Should the nickel be carried fairly high, the alloy must contain high silicon or manganese, or both, otherwise the hardness produced by nickel, chromium, and iron, irrespective of the lowness of the carbon content, is such that the alloy cannot be machined.

Chromium and iron, as described by the author, have the hardening properties brought about by high-temperature heating and fairly quick cooling, which are a serious drawback to the commercial development of this material. Sheets rolled from such alloys quickly harden, because of the rapid cooling when in contact with the rolls, therefore sheets can be successfully rolled only at high temperatures; and finishing sheets at high temperatures is difficult and adds materially to the cost. It is usual to finish sheets at or around a black temperature; at which temperature an alloy of about 12 or 13 per cent. chromium with very low carbon would have hardness.

The addition of silicon enables sheets to be turned out with just about the same ease that iron sheets can be produced. As a matter of fact, it is desirable to roll this material at black temperatures. Peculiarly enough, chromium alloys of 17 to 18 per cent. with carbon very low, say about 0.07 per cent., and with about 1 per cent. silicon, have a high degree of malleability at temperatures around 1000° to 1200° F. This property of this non-corrosive material is particularly useful for the manufacture of sheets as the finished rolling can be done at this temperature and a fair amount of elongation and reduction given to the sheet. No special precautions therefore need to be observed in rolling this grade of sheet. Hot pressing can be easily and expeditiously done on the finished sheet and the rapid cooling of the sheet when in contact with the die has no affect at all on the sheet. It does not stiffen it up materially because of the falling of temperature. The great malleability around these temperatures enables stampings to be readily made. Silicon also confers the property of great malleability at temperatures of 300° and 400° F.; in fact this type of alloy has better deep-drawing qualities than any non-corrod-

ing iron I have seen. The non-homogeneous nature of the chrome-iron alloy that has been annealed to produce softness does not add to the ease of machining, whereas the homogeneous nature of the alloy with the silicon increases the machineability.

There is a tremendous field for the use of rust-resisting irons. The figures prepared, a year or two ago, by Sir Robert Hadfield on the loss by corrosion have a tendency to make us gasp. No matter how much we may be opposed to using comparatively expensive materials for structural purposes, we are going to get into it deeply because of the constant cost of protecting iron.

The scale-resisting and the rust-resisting properties of iron and chromium are not due so much to the effects of chromium and iron as an alloy as they are to the scale film that forms upon the surface of the alloy. It is well known that aluminum is easily corroded, although it is considered by many to be a very excellent non-corroding material. As a matter of fact it corrodes more quickly than many metals. The surface takes on a transparent film of alumina, which is non-porous and protects the under surface from corrosion. Iron, when rusting, takes on a surface of iron oxide that is very porous and lets moisture through it to attack the iron underneath and as iron oxide is electronegative to iron a lively galvanic cell is set up.

As the author states, chromium and iron oxide, being the oxide of both iron and chromium, is also electronegative to the underlying metal, therefore corrosion is bound to take place where electrolysis is a factor. Under these circumstances, there is practically no difference between the polarity of iron oxide and iron and chromium and iron oxide as found on the author's stainless iron and steel; therefore it must be the non-porous nature of the oxide that forms upon the surface of these alloys that is the cause of preventing further corrosion.

An interesting experiment can be made to prove quickly the protecting oxide-film theory. If a surface of a rust-resisting iron, such as the author refers to, is polished for metallographic examination, so that the surface has a very high polish, and one-half of the surface is quickly covered with a film of oil which is let remain for a minute or so, the whole washed off in acetone, and water vapor allowed to condense upon the surface of the polished material, it will be found that the moisture will remain condensed upon the surface that was not covered with the oil film very much longer than upon the surface that was protected by the oil, showing that the surface not protected is already roughened and has greater ability to hold moisture upon its surface. If the specimen is let stand a few minutes longer, free from oil, probably 10 or 15 minutes, and the same experiment tried with water vapor, the line of demarcation will have entirely disappeared; both surfaces are in about the same roughened and oxidized condition.

Hot oxidation is an accelerated condition of ordinary atmospheric corrosion. If the temperature is raised sufficiently, the oxide becomes porous, because the iron oxide is the predominating oxide and may or may not separate from the chrome oxide, and the underlying surface of the metal quickly corrodes away, almost as badly as iron does at a lower temperature.

If very high percentages of nickel are used with chromium and iron, such as the well-known nichrome, the breaking down of the oxide takes place at much higher temperatures. If silicon is used, the oxide is thinner than that of the straight chromium and much less porous and remains so for longer periods and to greater temperatures. Small amounts of silicon have a tremendous effect, enhancing the resistance to excessive oxidation at high temperature.

At atmospheric temperatures, the oxide formed upon the surface of a chrome-iron-silicon alloy is of different color to that of the chromium and iron, is more reflectant to light, and, as far as I have been able to ascertain, is thinner, tougher, and more durable. Furthermore, the oxide of a chrome-silicon-iron alloy is slightly electropositive in nature to the underlying material, so that when the alloy is rusted somewhat, even though the rust may not be readily discernible, this rust has a tendency to protect the underlying metal should the film be damaged.

It is difficult to ascertain definitely whether the oxide of chromium-silicon-iron is electropositive or electronegative, as the material does not readily rust. In fact, it is as near rust-resisting as anything I have seen, but the oxide brought about by temperatures when polished off in one place and an electrolyte smeared over the oxide and on the unoxidized portion, and a millivolt meter connected across it, will show that the oxide is electropositive although the scale naturally will give an opposite reading.

Cold work on a chrome-iron alloy of about 11 to 14 per cent. chromium produces rusting because the safety factor between that which will rust and that which will not is so small that the difference in potential brought about by cold work is sufficient to bring about rusting; therefore rust-resisting alloys should contain high chromium, and preferably high silicon, with low carbon and the safety factor should be greater so that, in the event of cold working, there is practically no tendency for the material to corrode away.

The physical test specimens of 11 to 12 per cent. chromium referred to by the author, when exposed to the atmosphere, quickly rust; whereas test specimens made from about 17 or 18 per cent. chromium, about 1 per cent. silicon, very low carbon, and the balance iron, after being pulled, broken, and submitted to the atmosphere, do not rust.

The author recommends pickling for surface preparation to withstand corrosion. In my opinion a pickled surface, that is acid corroded, is

one of the finest surfaces that can be produced on rust-resisting irons, being quite as good as a polished surface, provided the chromium content is high enough to impart to the surface a higher chromium content brought about by the selective action of acid pickling. In other words, pickling will remove iron from the surface if the right acid is used; if the wrong acid is used, chromium is removed from the surface. An acid can be used where the iron is removed and the surface materially increased in the chromium content so that the exposed surface is of decidedly higher chromium content than 17 or 18 per cent. original content. With a lower chromium content, such as about 12 per cent., the iron is such a predominating quantity that pickling by various acids does not seem to have the same affect of increasing the chromium content of the surface, unless the surface is tremendously marred by eating out the iron to such an extent that the surface is rough to the hand; even then I have found that the surface will corrode. Polishing is better than pickling where a lower chromium content is employed as the surface on which the oxide forms is smooth to start with and it adds to the non-porous nature of the oxide that forms on the surface; I believe that is the only reason polishing is an advantage. I do not mean to say that polishing on 17 or 18 per cent. chromium with high silicon is not a good thing; it is, but it is not essential and is advisable only from the point of view of appearance.

About 50 per cent. higher chromium content than the author's 12 per cent. is preferable from a rust-resisting point of view; with the higher chromium content, a solvent of some type is essential to produce a satisfactory alloy from all points of view, therefore the author may prefer the 12 per cent. chromium analysis on the basis that it is good enough and about all the chromium he wants to handle in the alloy.

BERAM D. SAKLATWALLA,\* Bridgeville, Pa.—What has been known as stainless steel is a special application of high-chromium steel to cutlery purposes. The carbon ranges or the chromium ranges were not specified because they are *per se* of any intrinsic merit, but because, for the special purpose of a cutlery blade, it has been claimed by Brearley that steel containing less than 11 or 10 per cent. chromium does not show sufficient stainless properties and above 14 per cent. chromium tends to make the cutlery blade soft.

Mr. Armstrong has shown that low-carbon high-chromium iron is capable of hardening; the author shows that this is not the case. Is it not possible that we are failing to take into consideration other elements that may be present, for instance, in the case of the Armstrong composition, silicon, which might have a secondary effect in influencing hardness by heat treatment.

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\* General Superintendent, Vanadium Corpn. of America.



Mr. Armstrong has pointed out the good effect of silicon. Going up to higher chromium contents, I would say that the higher the chromium content, within certain limits, the better, the more resistant, the iron or steel is. If we are not confined to the cutlery business, it is proper to increase the chromium content; and if there are any physical difficulties in the fabrication of this steel they can be obviated by the addition of other elements such as silicon.

The theory of heterogeneity producing corrosion refers to a more or less secondary phenomenon. No doubt there is galvanic action when carbides are present, but in the case of rustless iron, where we are dealing with solid solutions only, the electrolytic theory is of minor importance. The addition of copper to high-chromium steel makes it acid-resisting besides improving the rust-resisting qualities.

While great credit has been claimed by Great Britain for pioneering in the field of rustless metallurgy, such is not entirely the case. The work that has been done by investigators in this country and also by Monnartz, Borchers, and others in Germany, is far prior to any work on rustless metallurgy that has been developed in Great Britain along the lines of the Brearley patent. What Great Britain has accomplished, and what it can claim pioneering credit for, is the application of rustless steel to cutlery.

With regard to the engineering development of rustless iron, one fact that has materially hindered its progress is its high cost of production. However, within the last two or three years considerable attention has been paid to the question of producing high-chromium iron by more economical processes, and today in this country as well as in Great Britain, chrome-iron processes are developed in a commercial way by direct reduction of chrome ore into the molten steel without the use of low-carbon ferrochromium and without using carbon as a reducing agent.

JOHN H. G. MONYPENNY (author's reply to discussion).—Mr. Armstrong's remarks contain so much that is of doubtful accuracy that to reply in any detail to his contribution would take up too much space. It may be an advantage, however, to deal with a few of the points raised.

Mr. Armstrong refers to the investigations published by Monnartz and other early investigators, but his remarks suggest that he is imperfectly acquainted with the results of their work. A discussion of such work, however, would take too much space and is, moreover, outside the scope of the author's paper.

Mr. Armstrong's remarks on the carbon content of stainless steel are confused and indicate that he does not thoroughly appreciate the action of this element. Carbon is required in varying amounts in stainless steel for the purpose of producing material of different intrinsic hardness,

just as it is in ordinary steel, and one can, for example, no more make a satisfactory cutting tool (*e.g.*, a knife blade) out of the very low-carbon stainless iron than one could from a piece of ordinary dead soft steel. There is a notable difference, referred to in the paper, in the effect of carbon in stainless and ordinary steels respectively in that its power of producing "steel" from "iron" is about three times as great in the case of the high-chromium steel as it is in the ordinary steel. For this reason it is impossible to argue, from the results obtained on quenching stainless iron containing approximately 0.07 per cent. carbon, that chromium-iron alloys absolutely free from carbon would harden in a similar manner. An ordinary carbon steel containing 0.15 to 0.20 per cent. carbon can be hardened quite appreciably by suitably quenching small samples, but no one would argue, therefore, that pure iron would also harden. Yet the stainless iron mentioned above has structurally the same proportion of ferrite and pearlite as the mild steel. Mr. Armstrong's statement that such low-carbon stainless irons contain as much carbide when quenched from high temperatures as when annealed is obviously incorrect to anyone who has examined such alloys microscopically. In the same way, the use of material containing about 6 per cent. carbon, which apparently Mr. Armstrong regards as the best amount of carbon to have in stainless material if there is to be any at all, might have some chance of success if many engineering applications could be found for a material having mechanical properties somewhat akin to those of white cast iron. Incidentally, the chromium content of such alloys would probably have to be of the order of 40 or 60 per cent. in order to obtain corrosion-resisting properties.

Mr. Armstrong's statement that low-carbon high-chromium steel was produced before 1920 (the date on which the company with which the author is associated produced it commercially) is in a sense correct. A few such alloys had been produced but only on experimental lines; the author's firm, for example, made such an alloy in 1915. The reference in the paper, however, was to the production of the alloy on a commercial scale as an article definitely on the market, a vastly different thing from making an experimental alloy.

Mr. Armstrong's statement that the addition of 1 per cent. silicon to a stainless iron prevents the latter from hardening when quenched from high temperatures is quite wide of the mark; such an addition of silicon raises to a considerable degree the carbon change point of stainless steels and irons, and therefore the temperature necessary to harden them, but when quenched from a temperature high enough to clear this raised point they harden in a manner similar to that of other steels.

Few who have studied corrosion at all will agree with Mr. Armstrong's statement that hot oxidation is an accelerated condition of ordinary atmospheric corrosion; and his remarks on the rolling of sheets made of

stainless iron suggest that he is only imperfectly acquainted with the hot working of that material.

Mr. Saklatwalla appears to have misread the author's remarks regarding the hardening of low-carbon high-chromium iron. The results given in the paper showed that two such irons on quenching had tensile strengths of about 73 and 85 tons per square inch respectively, corresponding to Brinell hardness number of about 340 and 387.

## Effect on Steel of Variations in Rate of Cooling in Ingot Molds

BY WILLIAM J. PRIESTLEY, PITTSBURGH, PA.

(New York Meeting, February, 1924)

MUCH time has been devoted, by metallurgists, to the study of steel after solidification and remarkable strides have been made in the heat treatment of steel, but less knowledge is available of the thermophysical activity of the constituents of steel prior to solidification in the mold. It is known that certain elements added to steel produce marked changes in physical properties, also that other elements added to steel produce similar changes, but we have only meager knowledge as to how these elements combine in steel under different conditions of solidification.

It is not sufficient to know, from chemical analysis, that a certain element is present in steel. We should know how this element is in combination with the other elements and whether the combination is such as will give the greatest physical properties. Certain elements go into solid solution with the iron, while others segregate to the grain boundaries and combine with the impurities collected there. Until it is known where an alloy produces the most beneficial effect and a means is determined for controlling its physical location by altering solidification conditions, or otherwise, we will not obtain the maximum value from our alloys.

When molten steel freezes, it forms a heterogeneous mass of various crystalline constituents; and as the transformation of steel from a liquid state to the solid crystallized state is a critical step, involving as great a transfer of heat as any other operation in the making of finished steel, a variation in the rate of this heat transfer will have much to do with the arrangement of the various constituents in the solid state. The object of this paper is to show some of the effects on steel caused by variations in the rate of cooling in the ingot mold, particularly as to ingotism, segregation, dendrites, and intergranular material.

## CRYSTALLIZATION FROM LIQUID STATE

Steel is generally cast in sand or cast-iron molds. The former produce a slow cooling, while the latter are intended to conduct the heat very rapidly from the molten metal. When carbon steel is teemed from the ladle into the mold, it is a solution of pure metal and non-metallic substances, chiefly iron, carbide of iron, oxide of iron and manganese, silicate of iron and manganese, phosphide of iron, sulfide of iron and manganese, and traces of alumina, together with carbon monoxide, hydrogen and nitrogen gas.

Rosenhain, Desch, and others have shown that when metals pass from the liquid to the solid state, the process of solidification results in crystallization of various forms and sizes, depending on the rate of cooling. Each crystal grows, simultaneously with a multitude of others, from its own center through a building up of metal from the liquid surrounding it. Certain elements go into solid solution and combine with the iron to form the crystals. Other elements, with impurities and non-metallic substances, segregate to the grain boundaries, and solidify to form a film of amorphous cement, that, in commercial steel, produces lines of mechanical weakness.

## FORMATION OF DENDRITES AND OCTAHEDRAL CRYSTALS

The crystalline grain growth in ingots poured under extreme conditions, in so far as the rate of cooling the steel was concerned, is shown in Figs. 1, 2, and 3, which represent the steel as cast without annealing. The steel in each case is nickel-chrome of approximately the same composition; namely, 0.40 per cent. carbon, 3.5 per cent. nickel, and 2 per cent. chromium. The steel shown in Fig. 1 was poured into an iron mold with a chill of about 5 to 1; that is, the area of the surrounding mold was five times the cross-sectional area of the ingot. As shown in Fig. 1, a dendritic structure extends from the outside of the ingot to the center. The metal was cooled very rapidly from the molten state to below the granulation zone, thus preventing the formation of octahedral crystals.

The ingot shown in Fig. 2 was cast in an iron mold with a chill of 3 to 1. Because of the less rapid withdrawal of heat, the dendrites extend only about  $1\frac{1}{2}$  in. from the surface; beyond are the coarse octahedral crystals caused by a slower cooling through the granulation zone.

The ingot shown in Fig. 3 was cast in a sand mold, with a wall 10 in. thick, with the least possible chill; this resulted in very slow cooling. The large octahedral crystals in the middle of the ingot show the original ingot structure; the metal surrounding this area has been refined by annealing, and is not considered in this discussion. The octahedral

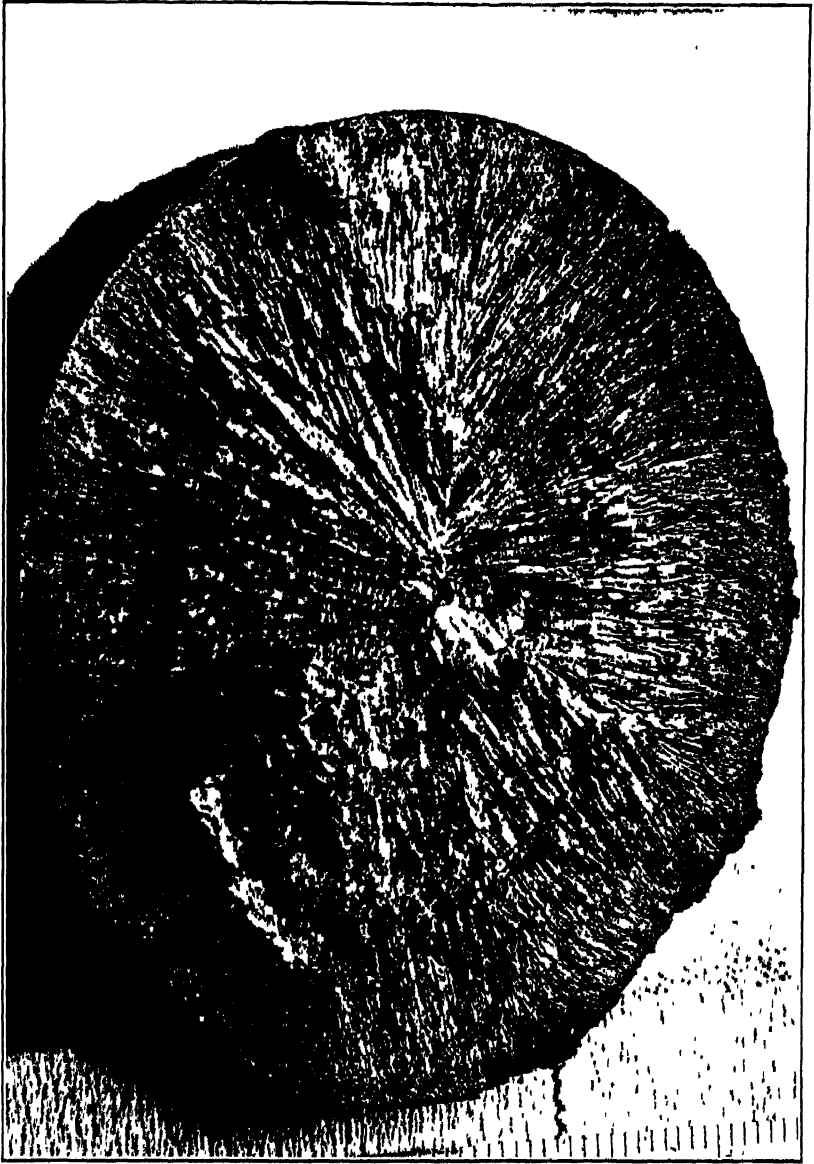


FIG. 1.—FRACTURE OF NICKEL-CHROME STEEL CAST IN IRON MOLD; MOLD AREA FIVE TIMES INGOT AREA. NOTE LONG DENDRITES WITH NO OCTAHEDRAL CRYSTALS. INGOT DIAMETER, 4 IN.; PHOTOGRAPH FULL SIZE.



FIG. 2.—FRACTURE OF NICKEL-CHROME STEEL CAST IN IRON MOLD; MOLD AREA THREE TIMES INGOT AREA. NOTE DENDRITES WITH OCTAHEDRAL CRYSTALS. INGOT DIAMETER 12 IN.; PHOTOGRAPH ONE-HALF SIZE.



FIG. 3.—SAND-MOLD CASTING WITH MINIMUM AMOUNT OF CHILL; NO DENDRITES, ALL OCTAHEDRAL CRYSTALS; LARGEST CRYSTALS  $\frac{3}{4}$  IN. DIAMETER.



crystals varied from  $\frac{1}{2}$  to  $\frac{3}{4}$  in. in diameter. This ingot cooled very slowly, even through the granulation zone, and the steel was held so long above the critical temperature that a secondary crystal growth took place.

#### EFFECT OF TEMPERATURE ON CRYSTAL-GRAIN GROWTH

A theoretical analysis of what takes place in the ingot mold during solidification of steel will explain why the ingot structure obtained in Fig. 1 is considered superior to the structure shown in Fig. 3.

Above the freezing point of molten steel, crystallization is very slow.



FIG. 4.—SECTION BROKEN FROM INTERIOR OF A SHRINKAGE CAVITY OF 100-TON ELECTRIC-STEEL CASTING, SHOWING PINE-TREE CRYSTAL FORMATION.

Only a few crystal centers, or nuclei, exist and the solidification of the metal from a high temperature results in the formation of only a few crystals, which become very large. As the temperature of the liquid drops, the rate of formation of crystal centers increases and, within a given space, the growth of each crystal is proportionally limited in size. Therefore, the lower the temperature from which crystallization starts, the greater will be the number of crystal centers and the smaller will be the dendrites or octahedral crystals.

When the steel in Figs. 1 and 2 came into contact with the wall of the iron mold, the temperature dropped suddenly, because of the chilling effect, or rapid transfer of heat from the metal to the iron mold. Crystals began to form at an infinite number of centers or nuclei along the surface of the mold. For a fraction

of a second, this crystal growth probably looked like that shown in Fig. 4, which shows small "pine tree" crystals growing toward the center of the mold and normal to its surface. The number of crystal grains multiplied so fast and the grains were so close together that it was possible for them to grow only in one direction, toward the center of the ingot. This resulted in the formation of the fine dendritic structure appearing near the surface of the ingots in Figs. 1 and 2.

As the rate of absorption of heat by the mold decreased, fewer centers were formed; and while the dendrites continued to grow toward the center of the ingot, they were less crowded, and increased in width. After a time, as shown in Fig. 2, as the rate of cooling decreased and the temperature of the molten steel became more nearly uniform on all sides of the grain centers, the crystals were free to grow in all directions and became octahedrons instead of dendrites.

## EFFECT OF RATE OF COOLING ON SEGREGATION

Those impurities, or foreign substances, that do not combine with the iron to form a solid solution are rejected by the crystalline grains to their outer boundaries. When the crystals are small and numerous, the film surrounding them is thin; but as the crystals increase in size, the segregation is greater and the film becomes thicker. This envelope is composed of varying amounts of ferrite and cementite (depending on the rate of cooling through the dendritic, granulation, and critical zones) also alloying elements and inherent impurities, such as phosphides, sulfides, the various forms of silicates, oxides, and gases that exist to a greater or less extent in all steels.

It has been demonstrated, by the use of the microscope and other mechanical testing devices, that where large amounts of impurities are segregated around the crystal grains, the metal will have lower ductility and offer less resistance to fatigue than where the impurities are scattered more finely and uniformly throughout the entire structure. Therefore, anything that may be done during the solidification of the steel to scatter or distribute the impurities as uniformly as possible will improve the quality of the steel. One way of accomplishing this is to cool the steel rapidly and hasten solidification, which produces smaller crystals and prevents segregation.

In order to show the effect of the rate of cooling on segregation, six ingots, 8 in. in diameter and 18 in. long, were made from the same heat of steel, but with different rates of cooling. The ladle analysis of this steel was carbon 0.37 per cent., manganese 0.56 per cent., phosphorus 0.042 per cent., sulfur 0.041 per cent., silicon 0.32 per cent.

Ingot No. 1 was cast in an iron mold with a chill of about 5 to 1; No. 2 was cast in an iron mold with a chill of 3 to 1; No. 3 was cast in an iron mold with a chill of 1 to 1. Ingot No. 4 was cast in a sand mold with a wall thickness such as to make the area of the mold equal to the cross-sectional area of the ingot; No. 5 was cast with the area of the mold three times the area of the ingot; No. 6 was cast with the area of the mold five times the area of the ingot. Fig. 6 shows the grain size in transverse fractures of this series of six ingots cast with different rates of cooling.

Sulfur prints taken from 4-in. bars forged from each of the six ingots are shown in Figs. 7-12. The three ingots cast in the sand show about the same degree of segregation, with a large non-metallic inclusion in the center. The last three sulfur prints show the result of cooling the steel slowly. Large non-metallic inclusions have segregated to the center of the ingot before the steel solidified; also the inclusions entrapped between the grain boundaries throughout the section are larger and less uniformly distributed than in the case of the three ingots cast in iron molds. The ingot from the mold having the 3 to 1 chill, Fig 8, has the finest and most

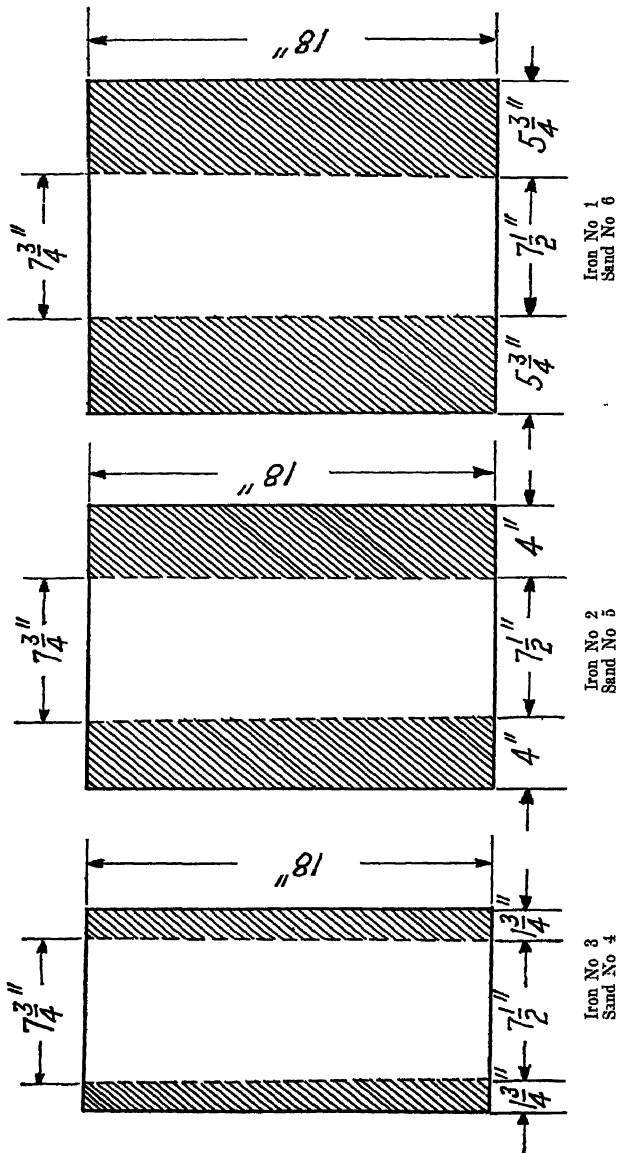


FIG. 5.—DIMENSIONS OF IRON AND SAND MOLDS.

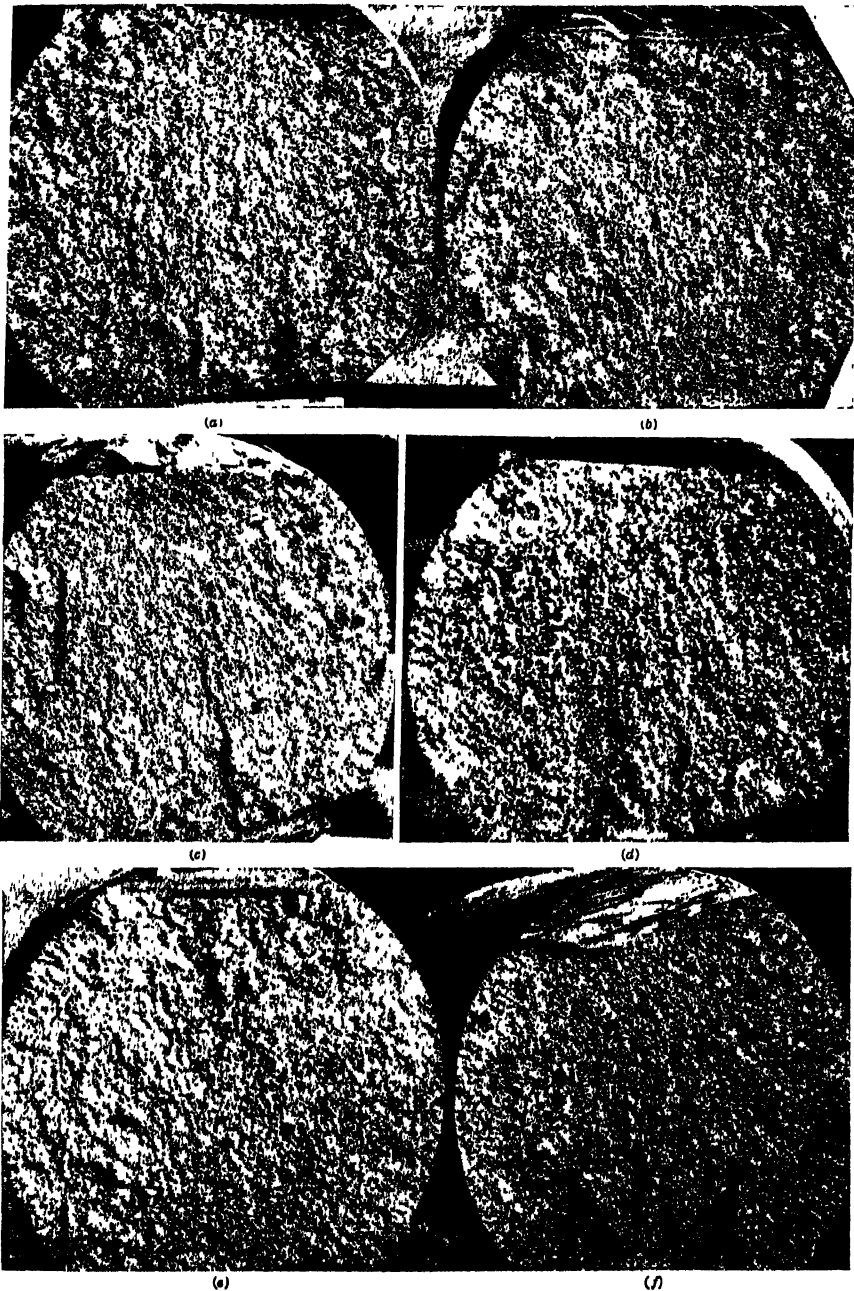


FIG. 6.—SERIES OF FRACTURES SHOWING GRAIN SIZE IN 8-IN. INGOTS CAST WITH DIFFERENT RATES OF COOLING (a) IRON MOLD AREA FIVE TIMES INGOT AREA, (b) IRON-MOLD AREA THREE TIMES INGOT AREA; (c) IRON-MOLD AREA EQUAL TO INGOT AREA; (d) SAND-MOLD AREA EQUAL TO INGOT AREA; (e) SAND-MOLD AREA THREE TIMES INGOT AREA, (f) SAND-MOLD AREA FIVE TIMES INGOT AREA.

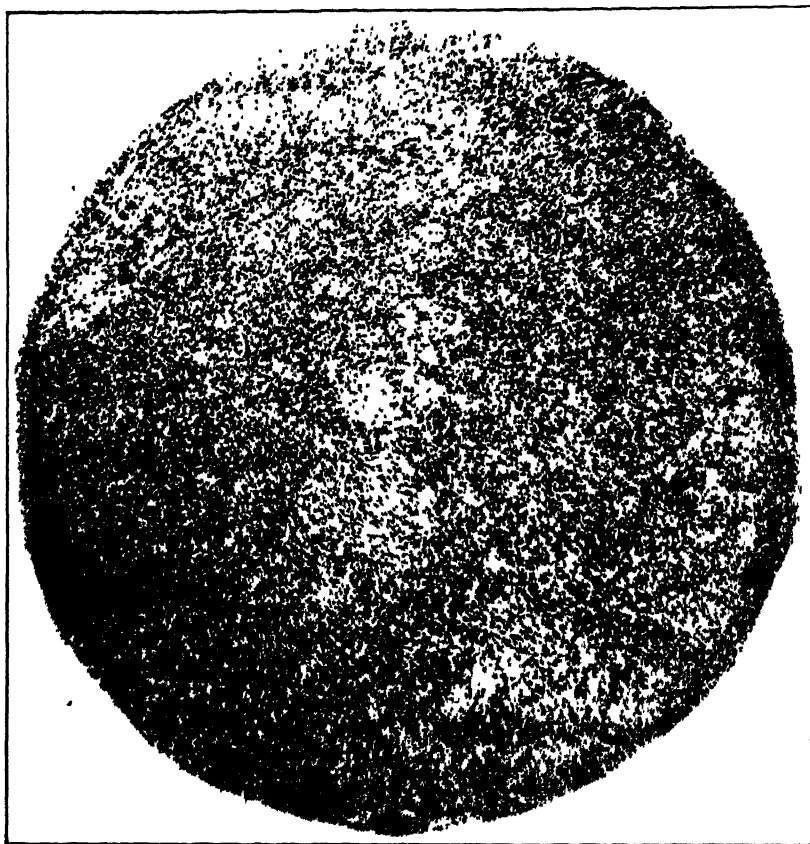


FIG. 7.—SULFUR PRINT OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN IRON MOLD HAVING AN AREA FIVE TIMES INGOT AREA.

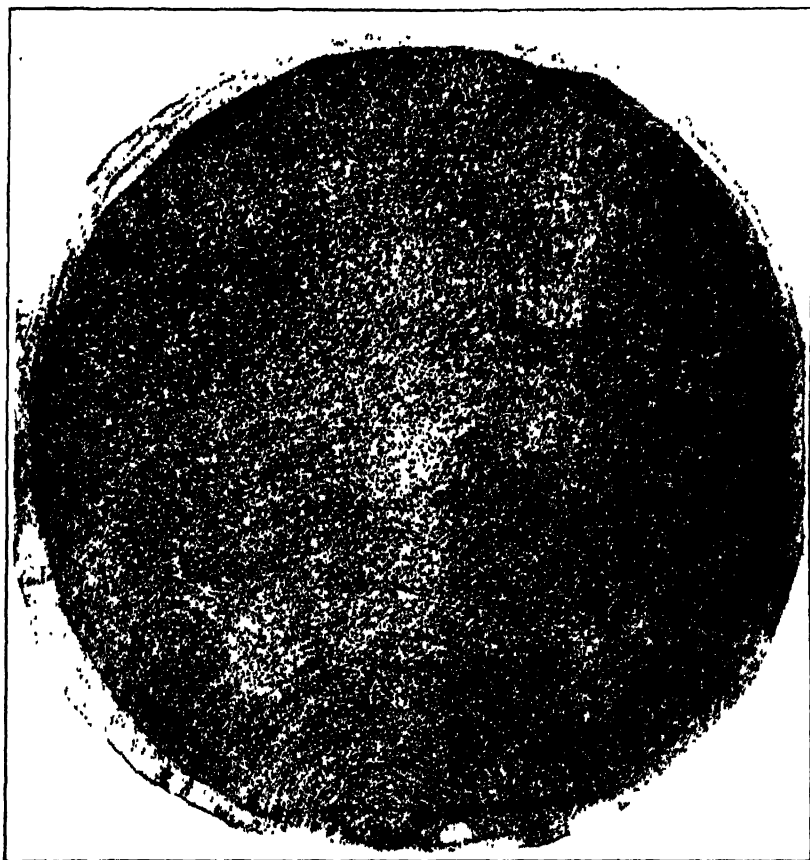


FIG. 8.—SULFUR PRINT OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN IRON MOLD HAVING AN AREA THREE TIMES INGOT AREA.

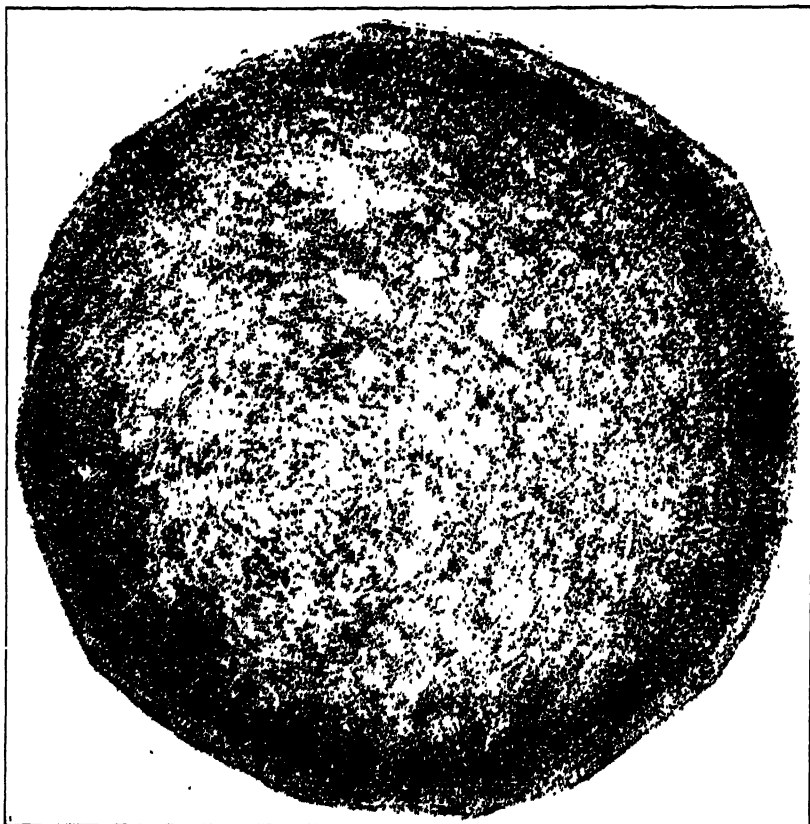


FIG. 9.—SULFUR PRINT OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN IRON MOLD HAVING AN AREA EQUAL TO INGOT AREA.

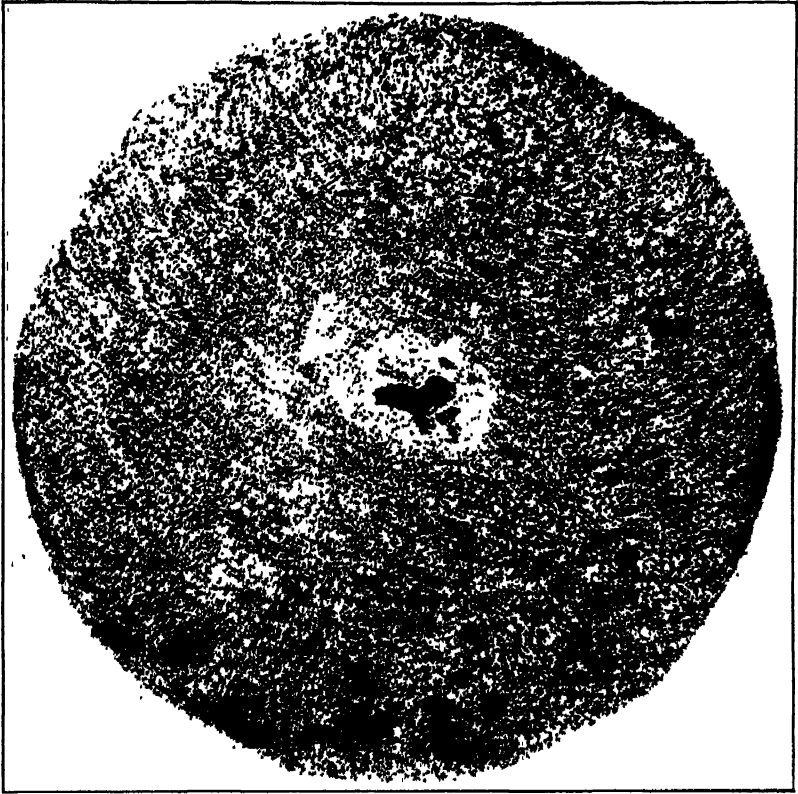


FIG. 10.—SULFUR PRINT OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN SAND MOLD HAVING AN AREA EQUAL TO INGOT AREA.



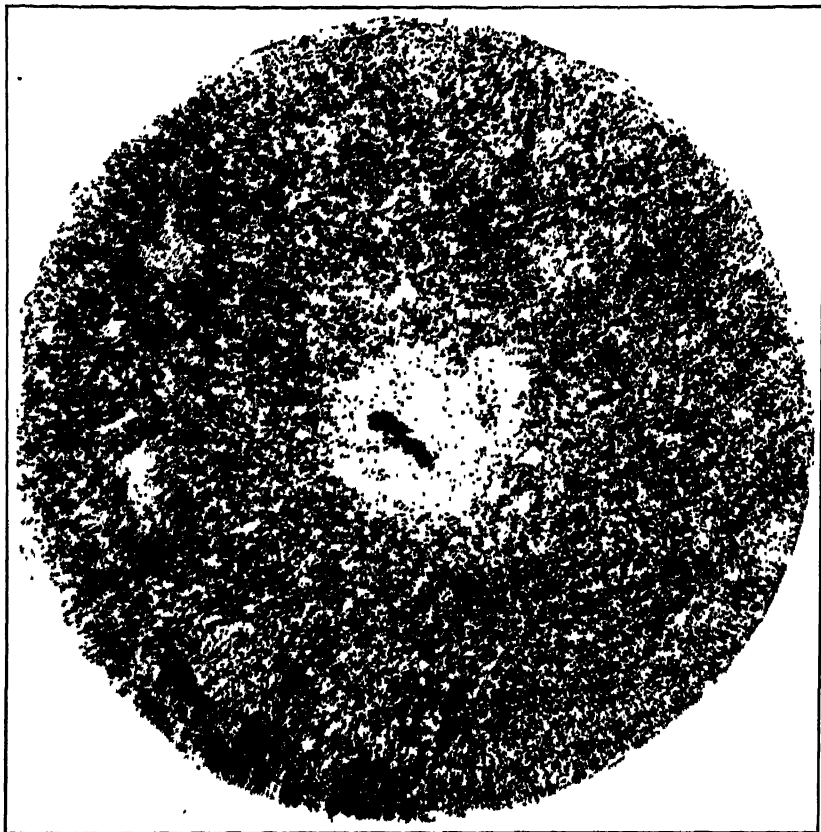


FIG. 11.—SULFUR PRINT OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN SAND MOLD HAVING AN AREA THREE TIMES INGOT AREA.

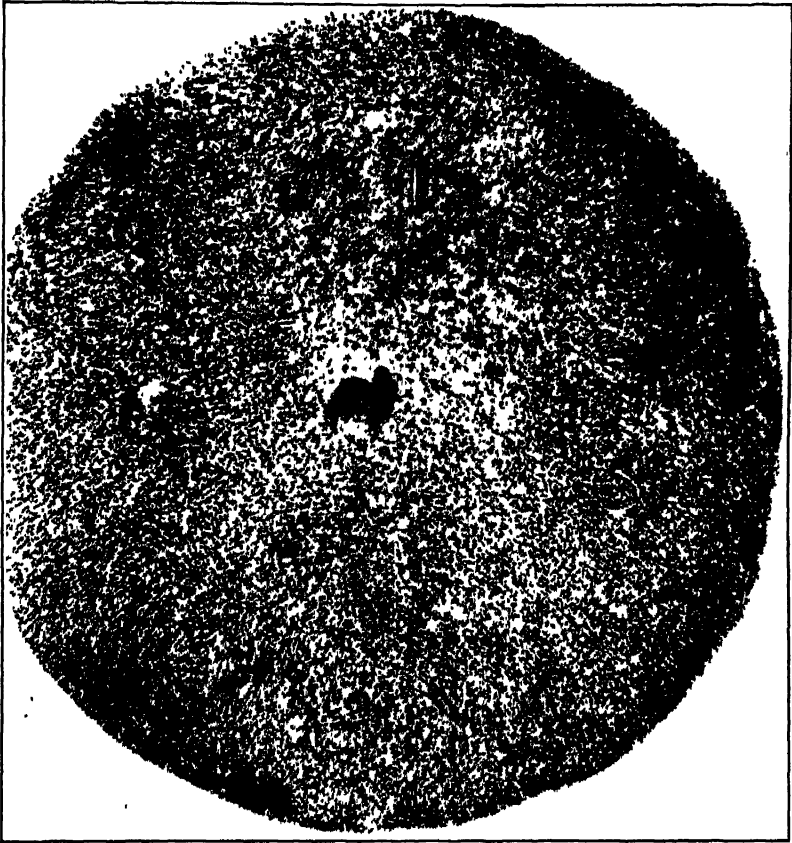


FIG. 12.—SULFUR PRINT OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN SAND MOLD HAVING AN AREA FIVE TIMES INGOT AREA.



FIG. 13.—ETCHED MACROGRAPH OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN IRON MOLD HAVING AN AREA FIVE TIMES INGOT AREA.

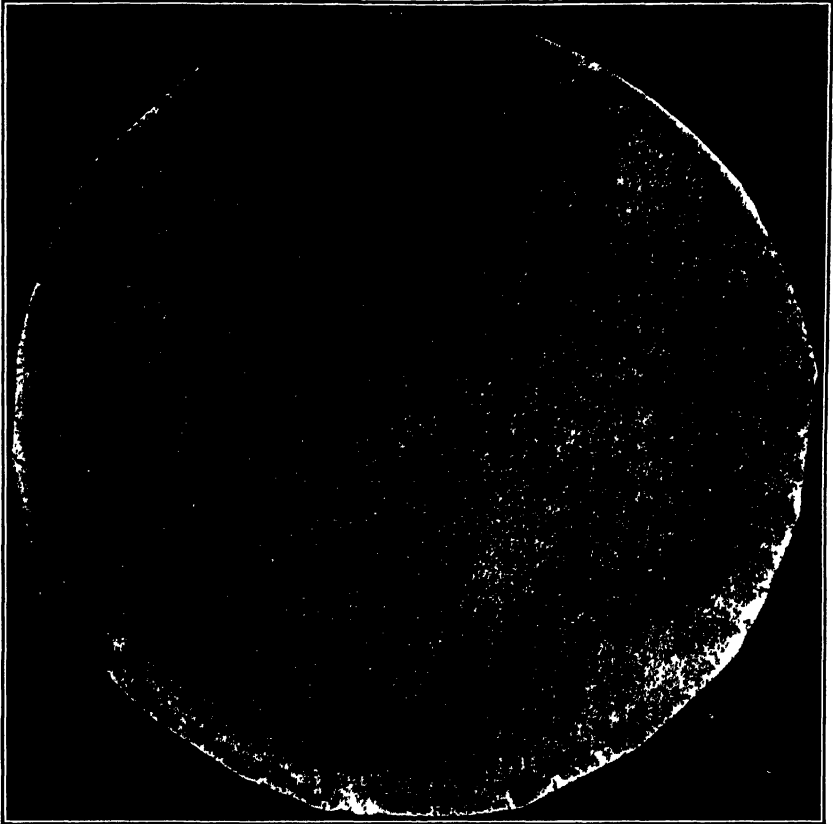


FIG. 14.—ETCHED MACROGRAPH OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN IRON MOLD HAVING AN AREA THREE TIMES INGOT AREA.

uniformly distributed inclusions. The ingot cast in the iron mold with the 5 to 1 chill, Fig. 7, has more segregation in the center than the bar from the 3 to 1 chill. This is probably because the thicker mold retarded the rate of cooling in the center of the ingot while the steel was passing through the granulating zone. The etched macrograph of this same bar, Fig. 13, also shows larger grain size than does Fig. 14, which is near the center of the section.

TABLE 1

Drillings from Billets	Location	Carbon, Per Cent.	Manganese, Per Cent	Sulfur, Per Cent.	Phosphorus Per Cent.
1	Center. . . . .	0 36	0 55	0 040	0 047
1	Halfway outside and center . . . . .	0 35	0 56	0.044	0.057
2	Center. .... .	0 41	0 56	0 044	0 052
2	Halfway outside and center . . . . .	0.38	0 55	0.044	0 058
3	Center. .... .	0.37	0 55	0 038	0.048
3	Halfway outside and center . . . . .	0.36	0 58	0.050	0 057
4	Center. .... .	0.54	0.54	0 042	0.046
4	Halfway outside and center . . . . .	0 39	0 58	0.040	0.051
5	Center. .... .	0.44	0 53	0 038	0 037
5	Halfway outside and center . . . . .	0 37	0 58	0 048	0 057
6	Center. .... .	0 51	0 56	0 046	0.051
6	Halfway outside and center . . . . .	0 39	0.58	0 050	0.055
1	Center . . . . .	0 36 to 0 37	0 54	0 041	0 043
1	Midway, 3 o'clock . . . . .	0.36 to 0 36	0 56	0 045	0 045
1	Midway, 9 o'clock . . . . .	0.36 to 0 37			
2	Center . . . . .	0 37 to 0 38	0 54	0 041	0 043
2	Midway, 3 o'clock. . . . .	0.33 to 0 39	0 55	0 045	0 047
2	Midway, 9 o'clock . . . . .	0.40 to 0 40			
3	Center . . . . .	0.37 to 0 38	0 55	0 044	0 044
3	Midway, 3 o'clock . . . . .	0.41 to 0 42	0 55	0 044	0 044
3	Midway, 9 o'clock . . . . .	0 38 to 0 39			
4	Center. .... .	0 37 to 0 37	0 54	0 039	0 040
4	Midway, 3 o'clock . . . . .	0 42 to 0 43	0 56	0 043	0 046
4	Midway, 9 o'clock . . . . .	0 39 to 0 40		0 042	0 042
5	Center. .... .	0 38 to 0 39	0 54	0 044	0 045
5	Midway, 3 o'clock . . . . .	0 40 to 0.41	0 56	0.042	0 045
5	Midway, 9 o'clock . . . . .	0 39 to 0.39		0.017	0.044
6	Center. .... .	0 43 to 0.44	0 54	0.041	0.040
6	Midway 3 o'clock. . . . .	{ 0 39 to 0 39 } 0.43 to 0.47	0.56	0 045	0.047
6	Midway, 9 o'clock. .... .	0.44 to 0 43		0 046	0.047

Table 1 shows the segregation of sulfur, manganese, and carbon, as determined by chemical analysis of drillings taken in the center and midway between the center and the outside of the bars shown in Figs. 7-12.

The chemical analysis shows that the dark spots in the center of the sand castings are not high manganese-sulfide inclusions, as might be assumed from looking at the sulfur prints; they are high carbon. These spots also show on the etched macrographs and are probably caused by a sorbitic structure in marked contrast with the light ring of hypocu-

tectic metal surrounding it. The chemical analyses show more plainly than the macrographs how very differently carbon, sulfur, manganese, and phosphorus segregate under different rates of cooling; manganese, sulfur, and phosphorus are less active in segregating than carbon after a certain temperature is reached during cooling, in the center of the ingot. The ladle analysis was 0.37 per cent. carbon, 0.56 per cent. manganese, 0.041 per cent. sulfur, and 0.042 per cent. phosphorus.

#### EFFECT OF RATE OF COOLING ON PHYSICAL PROPERTIES

To obtain a comparison of the physical properties of the heat of steel just referred to, when cast with varying rates of cooling in the mold, a longitudinal tensile bar was taken from each ingot, midway between the center and the outside. The first set of bars were taken from the ingots as cast and unannealed; these results are shown in Table 2. While these results are very irregular, the iron-mold castings show greater ductility, ultimate strength, and elastic limit. The bar from casting No. 2 broke outside the mark because of a flaw; as the casting was annealed before the bar was pulled, it was not possible to get a replacing bar.

TABLE 2.—*Results of Tests of Casting, Unannealed*

Casting Number	Tensile Strength, Pounds per Square Inch	Elastic Limit, Pounds per Square Inch	Elongation, Per Cent.	Reduction of Area, Per Cent
1	83,770	51,570	10 5	11 2
2	61,450	51,590	3	3 6
3	83,410	42,750	9 5	(Broke outside mark) 10 8
4	70,710		9	10.5
5	71,670	39,300	9 5	9 4
6	75,130	43,200	7	9 7

To determine what effect annealing would have on the physical properties of these same six ingots, they were placed together in the same furnace and given a thorough annealing at 1500° F. The results given in Table 3 were obtained on longitudinal tensile bars, taken midway between the center and the outside. A comparison of these results shows approximately the same ultimate strength and elastic limit on all ingots, but greater ductility on the iron-mold ingots with 5 to 1 chill and 3 to 1 chill. The coarse-grain structure in the sand-cast ingots was not fully broken up by annealing; also, the larger non-metallic inclusions impaired the ductility. The tensile bars were taken longitudinally from the upper end of the lower half of the ingots after fracturing midway between the top and bottom.

TABLE 3.—*Results of Tests of Casting, Annealed*

Casting Number	Tensile Strength, Pounds per Square Inch	Elastic Limit, Pounds per Square Inch	Elongation, Per Cent.	Reduction of Area, Per Cent.
1	76,990	38,790	17 5	27 2
2	79,590	39,790	19	24 1
3	78,040	39,940	16	18 2
4	75,700	37,300	15	18 3
5	76,600	37,690	12	17 1
6	76,950	38,850	15	18 6

The upper half of the ingots were heated and forged into bars 4 in. in diameter; they received a four to one reduction and were then thoroughly annealed together in the same furnace at 1500° F. Longitudinal tensile bars were then taken from the end of the bar that represented the bottom of the upper half of the ingot; these bars were drilled midway between the center and the outside surface. Results from these bars show improved physical conditions in all cases; the greatest improvement is in the ductility of the sand-cast ingots, because the coarse-grain crystals are broken down and the non-metallic inclusions around the grain boundaries are redistributed more uniformly in smaller particles.

TABLE 4.—*Results of Tests on Casting Forged 4 to 1 Reduction and Annealed*

Casting Number	Tensile Strength, Pounds per Square Inch	Elastic Limit, Pounds per Square Inch	Elongation, Per Cent.	Reduction of Area, Per Cent.
1	82,090	44,360	23	38 2
2	82,130	43,190	25	40 1
3	82,690	43,830	23	38.5
4	81,190	41,680	24	38.5
5	82,060	43,480	24	37 3
6	81,930	41,740	25	38.9

A similarity of results might be expected from longitudinal bars after forging and annealing. The mechanical work was sufficient to eliminate the difference in grain size that existed between the fast and slowly cooled ingots but it could not correct the evil effects resulting from the greater segregation in the more slowly cooled ingots. Had it been possible to take transverse tensile tests, the forgings made from the slowly cooled ingots might have shown an ultimate strength and elastic limit equal to the rapidly cooled ingots but the ductility would have been less. A comparison of the longitudinal sections of the test bars, Figs. 19 to 36, indicate that neither annealing nor forging have any appreciable effect in changing the magnitude or location of the solid non-metallic inclusions. These

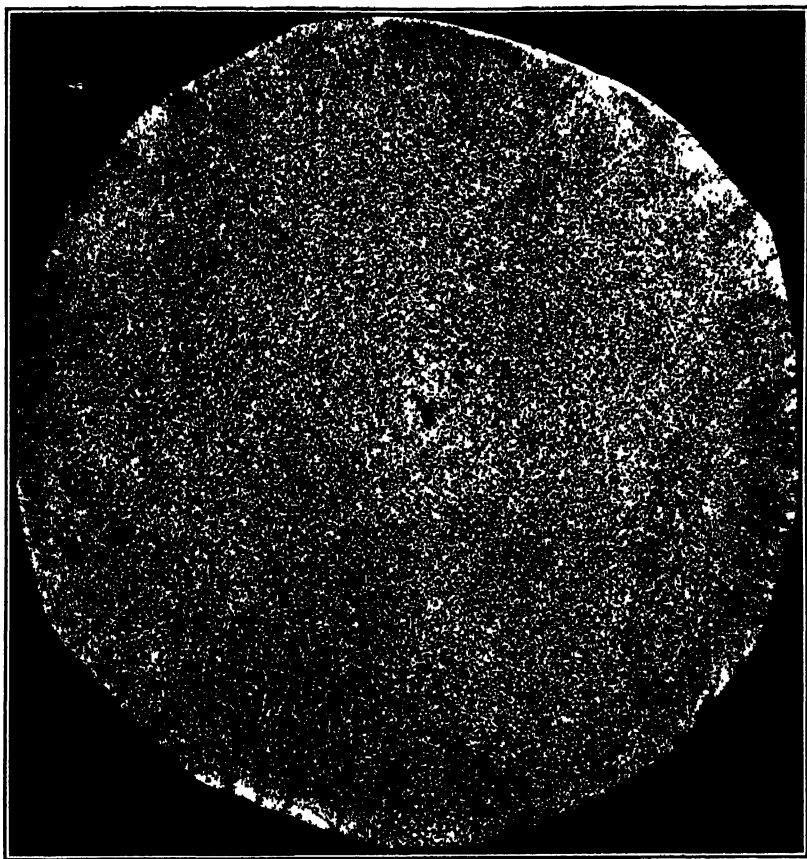


FIG. 15.—ETCHED MACROGRAPH OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN IRON MOLD HAVING AN AREA EQUAL TO INGOT AREA.



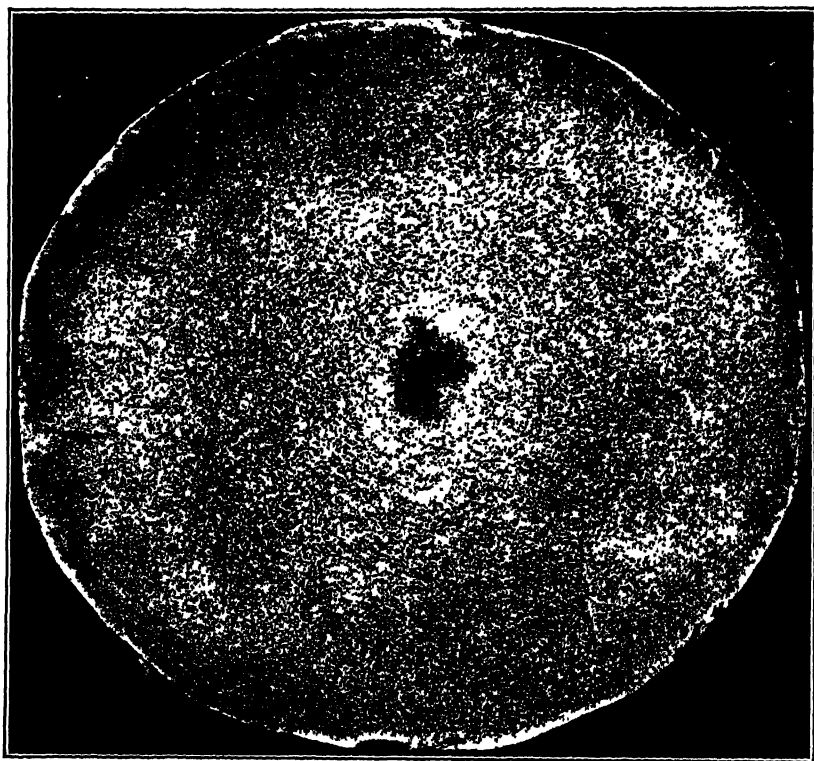


FIG. 16.—ETCHED MACROGRAPH OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN SAND MOLD HAVING AN AREA EQUAL TO INGOT AREA.

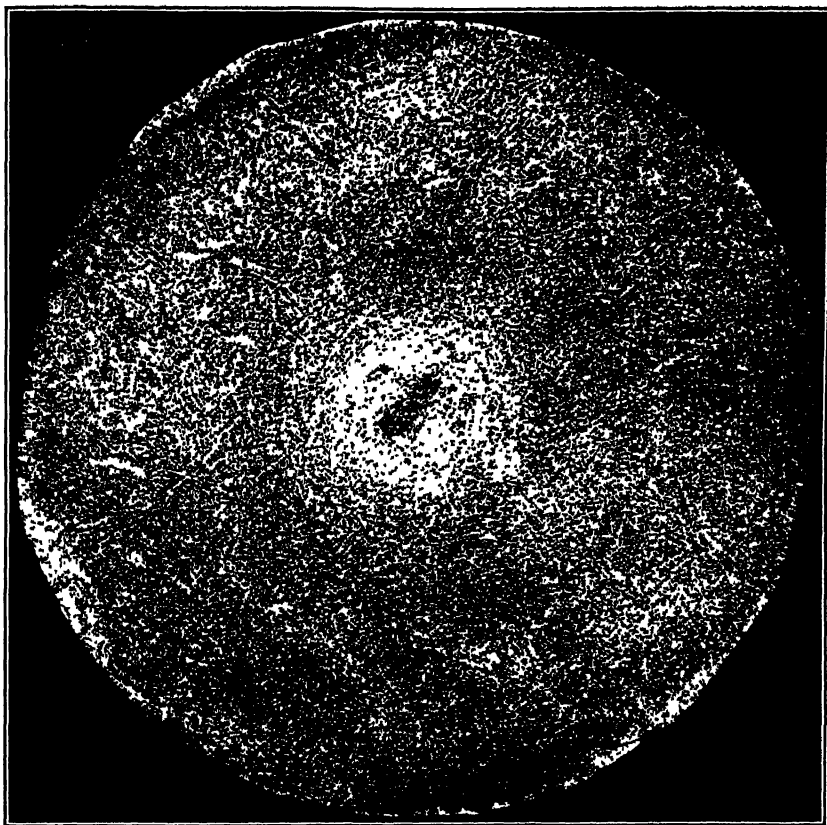


FIG. 17.—ETCHED MACROGRAPH OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN SAND MOLD HAVING AN AREA THREE TIMES INGOT AREA.

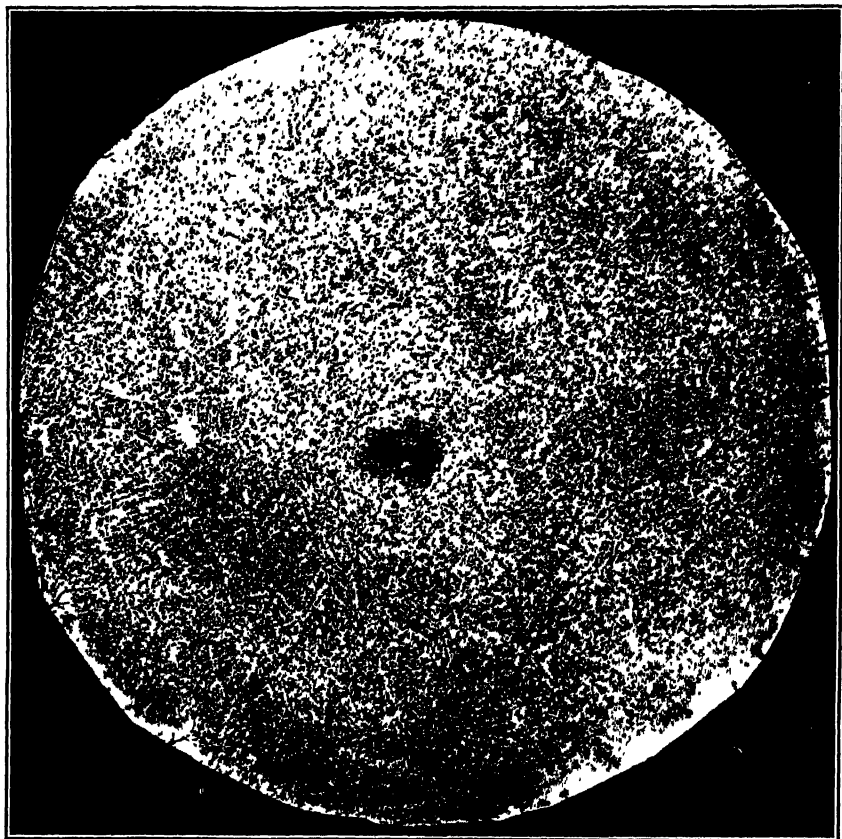


FIG. 18.—ETCHED MACROGRAPH OF TRANSVERSE SECTION OF 4-IN. BAR FORGED FROM INGOT CAST IN SAND MOLD HAVING AN AREA FIVE TIMES INGOT AREA.

sections also show that the solid non-metallic inclusions are smaller and more uniformly distributed in the iron-mold ingots than in the sand-mold ingots.

#### COMPARISON OF MACROSTRUCTURE ON INGOTS AFTER FORGING

While the longitudinal tensile bars taken midway between the center and outside of the series of forgings show practically the same tensile strength, elastic limit, and ductility, the macrographs of these forgings, when polished and etched with a solution of ammonium persulfate, show a marked contrast in the grain structure, corresponding to the various rates of cooling. The ingot made with the 3 to 1 chill in the iron mold, Fig. 14, contains the finest grain structure. The ingot made in the sand mold with the thickest wall, Fig. 18, shows the coarsest grain structure. The segregation at the center of the ingot is shown in these etched specimens; there is a slight indication of segregation in Fig. 15, which represents the 1 to 1 chill in the iron mold.

#### EFFECT OF MOLD DESIGN ON STRUCTURE

Wherever possible, in a forge shop or rolling mill, where the best quality of deoxidized steel is required, a selection of molds should be available, so as to apply the smallest mold possible for a particular forging or bloom. In small iron molds with the correct wall thickness, rapid cooling is accompanied by less grain growth and less segregation of impurities. This feature cannot always be worked to advantage, on account of the length of cuts or weights required in individual forgings or blooms. While in most specifications a minimum reduction of four to one is required from the ingot to the finished forging or bloom, in some cases a concession in reduction on the part of the customer would result in the production of better steel by the use of smaller ingots, free from ingotism and segregation.

Molds should be shaped so as to prevent planes of weakness forming where the ends of the dendritic crystals meet. Brearley<sup>1</sup> demonstrated this fact clearly in his experiments with both stearine and steel. The planes of weakness commonly occurring at the butt end of ingots may be overcome by using a round bottom in the mold, or a dish in the stool, instead of the usual flat stool.

Some steel men attribute the common transverse butt crack in the outside surface of big-end-down ingots to the strains set up where the vertical and horizontal dendrites meet. This crack may also occur when steel is poured so hot that the solidification at this point is retarded and the shell of the ingot is too weak to withstand the ferrostatic pressure

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<sup>1</sup> A. W. and H. Brearley: Some Properties of Ingots. *Jnl. Iron & Steel Inst.* (1916) 94, 137.

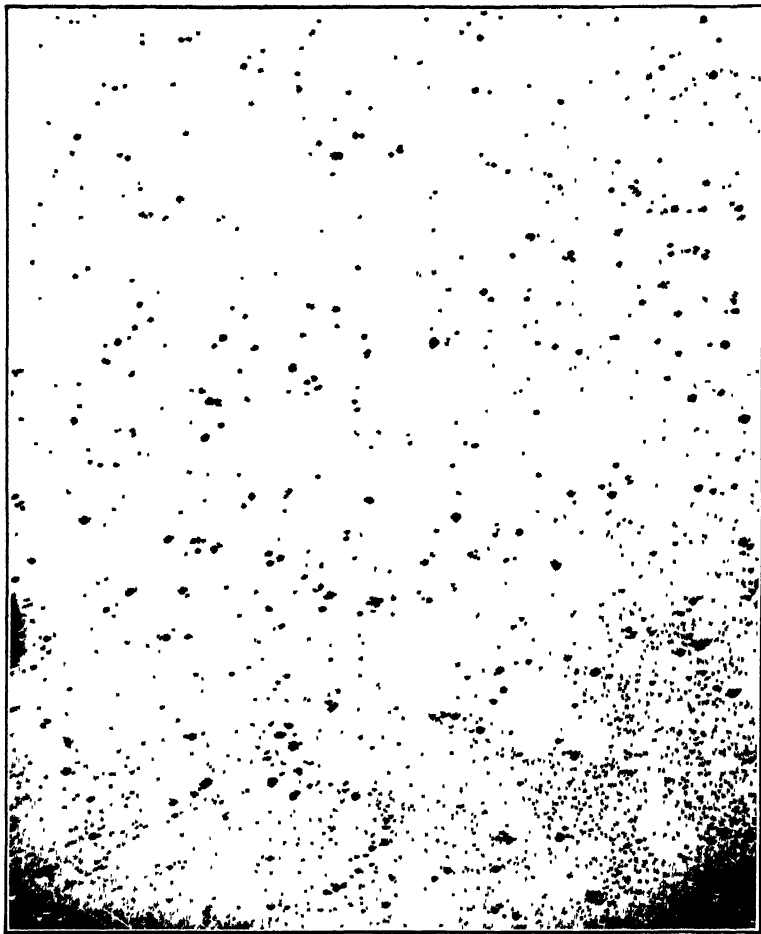


FIG. 19.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, UNANNEALED. INGOT WAS CAST IN IRON MOLD HAVING AN AREA FIVE TIMES INGOT AREA.  $\times 20$ .



FIG. 20.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TESTBAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, UNANNEALED. INGOT WAS CAST IN IRON MOLD HAVING AN AREA THREE TIMES INGOT AREA.  $\times 20$ .



FIG. 21.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, UNANNEALED. INGOT WAS CAST IN IRON MOLD HAVING AN AREA EQUAL TO INGOT AREA.  $\times 20$ .

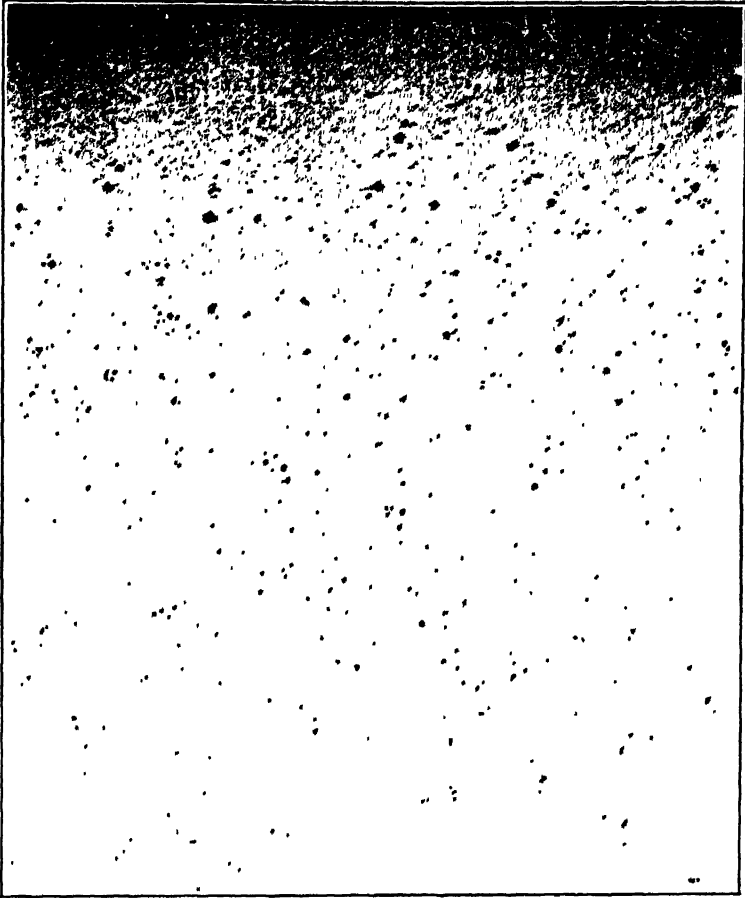


FIG. 22.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, UNANNEALED. INGOT WAS CAST IN SAND MOLD HAVING AN AREA EQUAL TO INGOT AREA.  $\times 20$ .



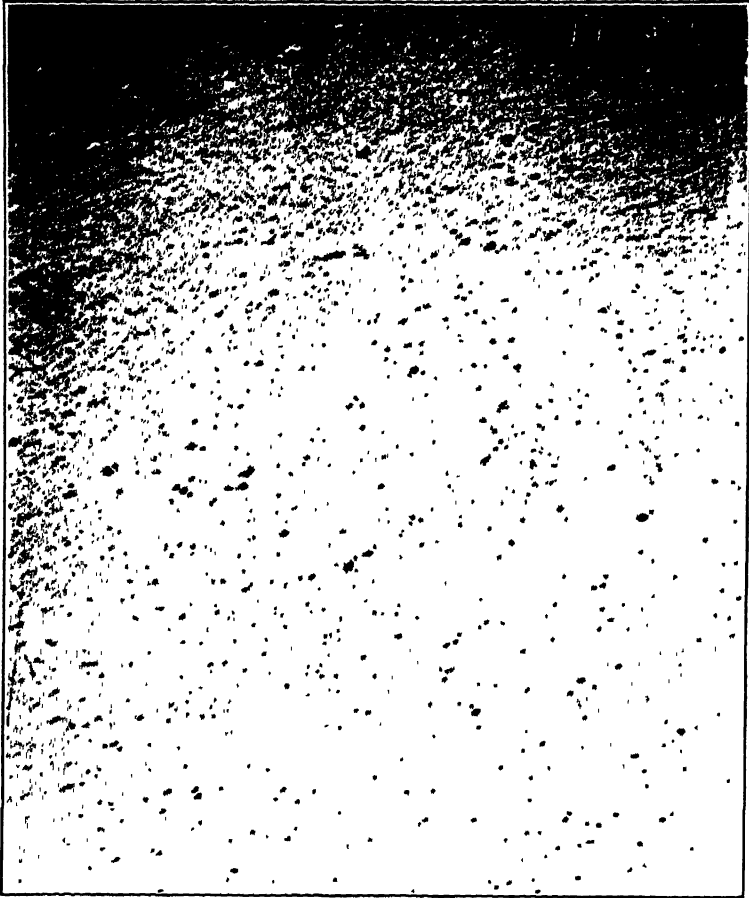


FIG. 23.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, UNANNEALED. INGOT WAS CAST IN SAND MOLD HAVING AN AREA THREE TIMES INGOT AREA.  $\times 20$ .

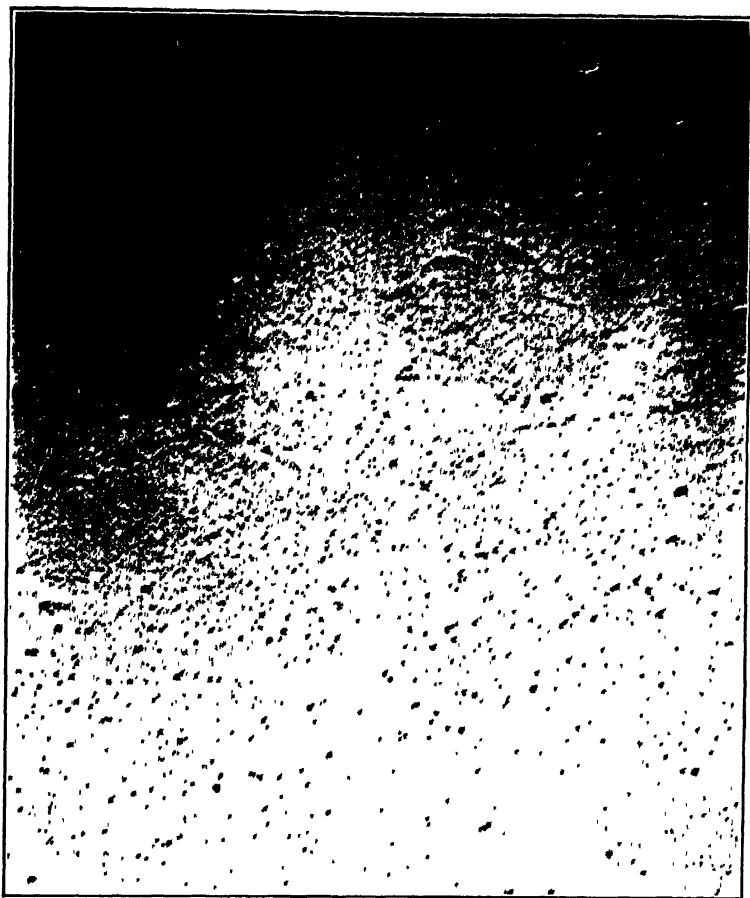


FIG. 24.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, UNANNEALED. INGOT, WAS CAST IN SAND MOLD HAVING AN AREA FIVE TIMES INGOT AREA.  $\times 20$ .

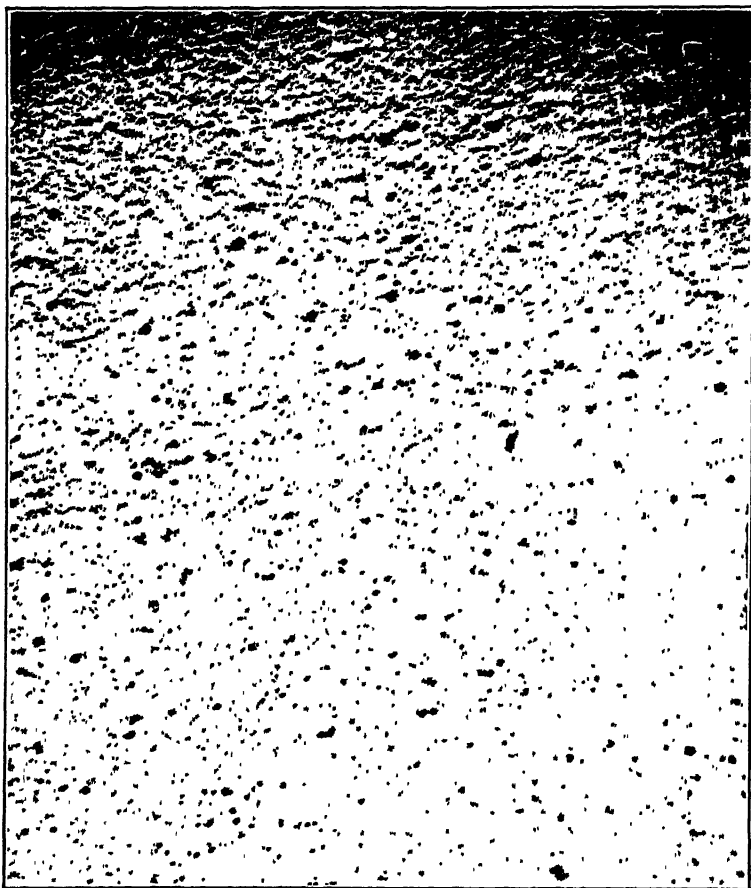


FIG. 25.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, ANNEALED. INGOT WAS CAST IN IRON MOLD HAVING FIVE TIMES AREA OF INGOT.  $\times 20$ .



FIG. 26.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, ANNEALED. INGOT WAS CAST IN IRON MOLD HAVING AN AREA THREE TIMES AREA OF INGOT.  $\times 20$ .

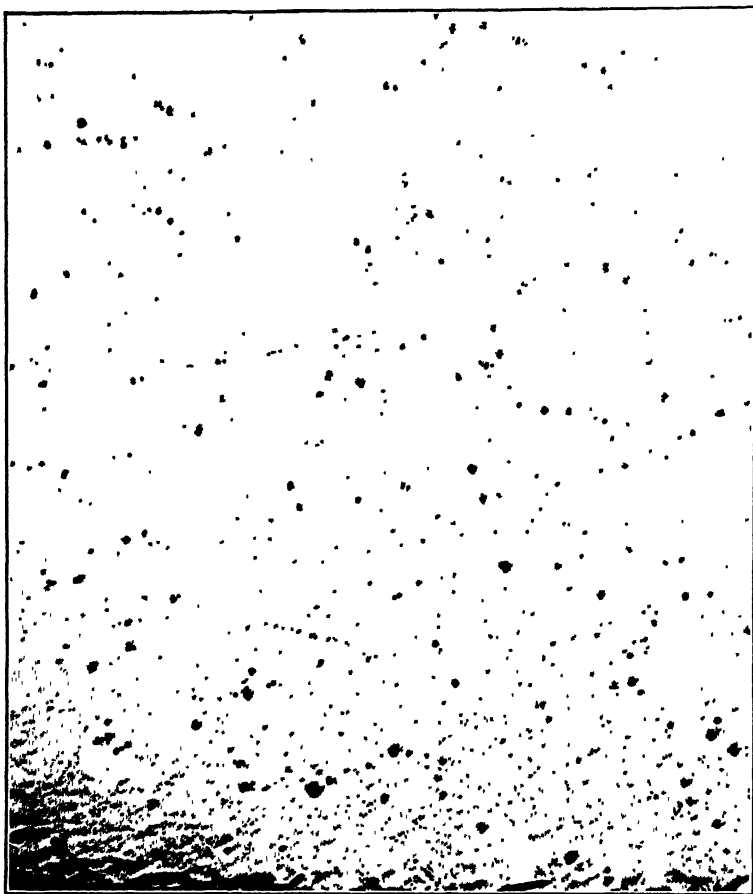


FIG. 27.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, ANNEALED. INGOT WAS CAST IN IRON MOLD HAVING AN AREA EQUAL TO AREA OF INGOT.  $\times 20$ .

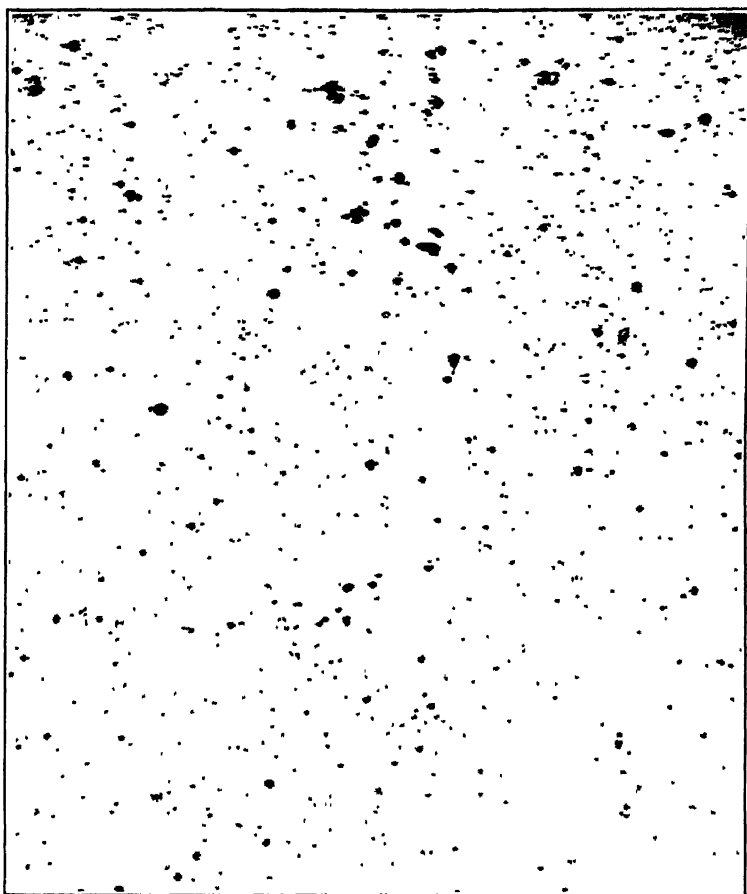


FIG. 28.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, ANNEALED. INGOT WAS CAST IN SAND MOLD HAVING AN AREA EQUAL TO AREA OF INGOT.  $\times 20$ .

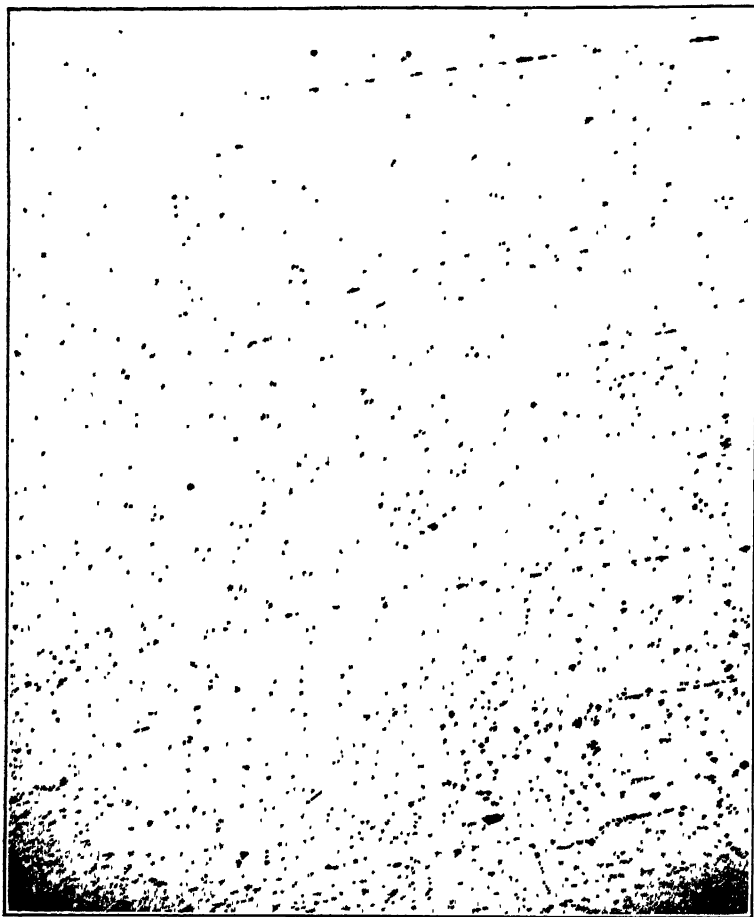


FIG. 29.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, ANNEALED. INGOT WAS CAST IN SAND MOLD HAVING AN AREA THREE TIMES INGOT AREA.  $\times 20$ .

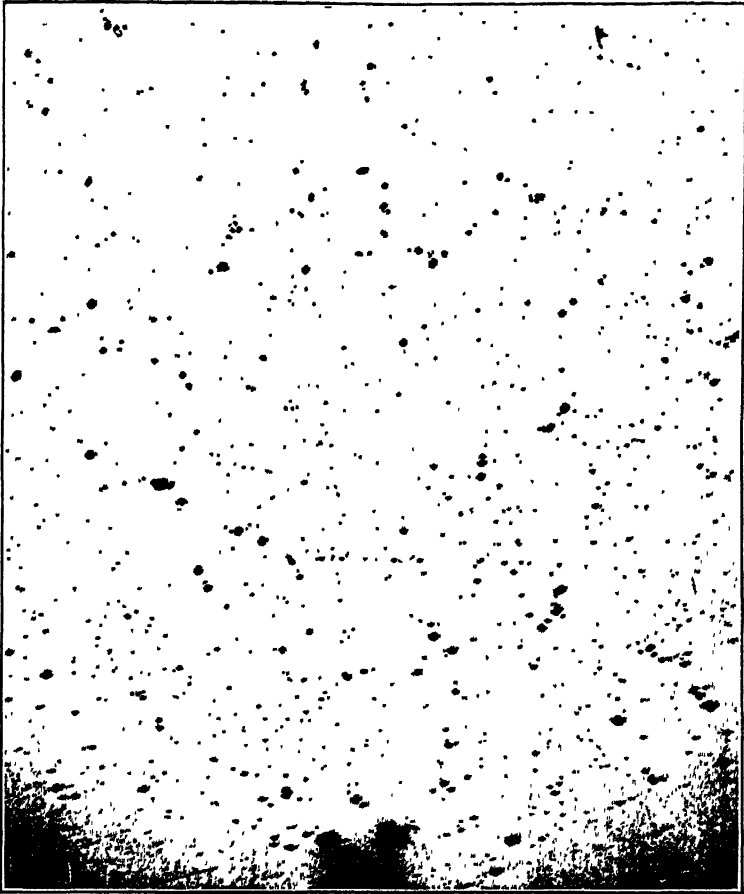


FIG. 30.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOT, ANNEALED. INGOT WAS CAST IN SAND MOLD HAVING AN AREA FIVE TIMES INGOT AREA.  $\times 20$ .



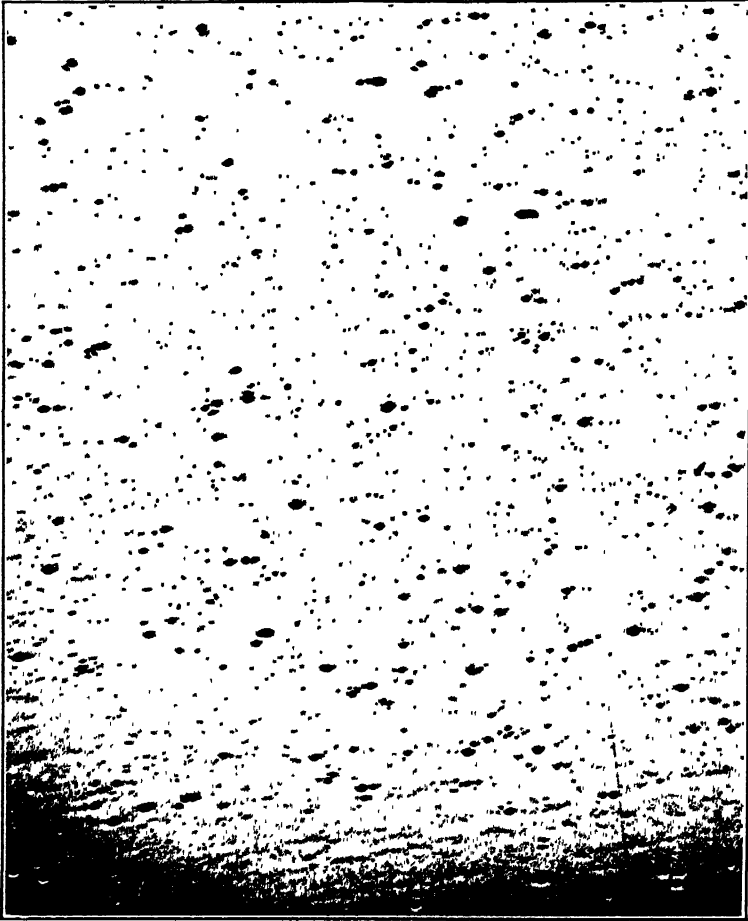


FIG. 31.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF FORGED UNANNEALED BAR. INGOT WAS CAST IN IRON MOLD HAVING AN AREA FIVE TIMES AREA OF INGOT.  $\times 20$ .



FIG. 32.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF FORGED UNANNEALED BAR. INGOT WAS CAST IN IRON MOLD HAVING AN AREA THREE TIMES AREA OF INGOT.  $\times 20$ .

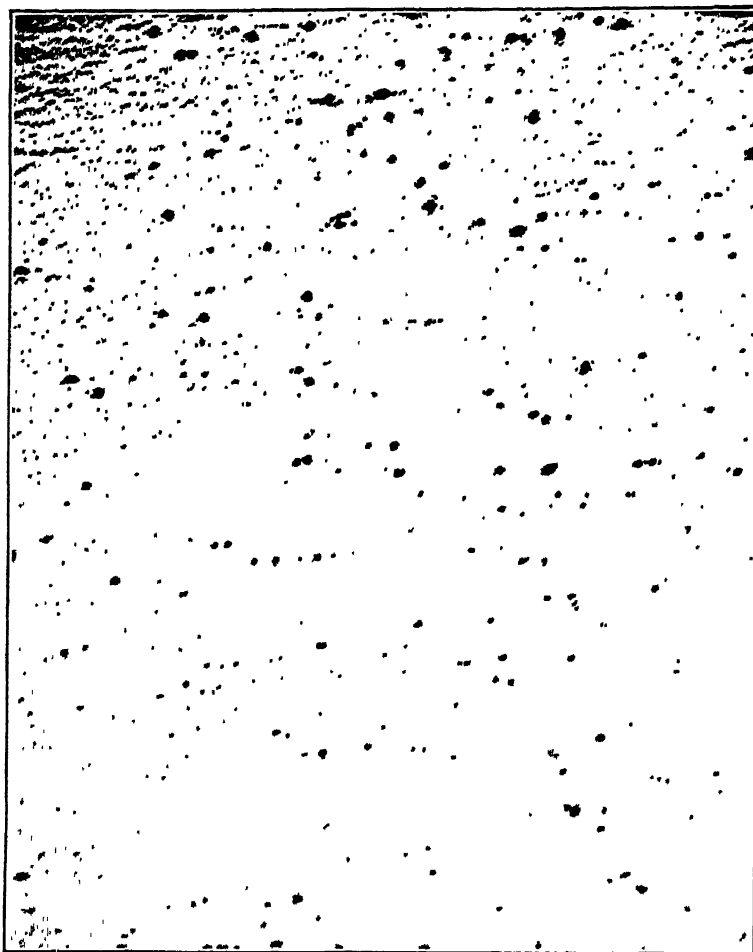


FIG. 33.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF FORGED UNANNEALED BAR. INGOT WAS CAST IN IRON MOLD HAVING AN AREA EQUAL TO AREA OF INGOT.  $\times 20$ .

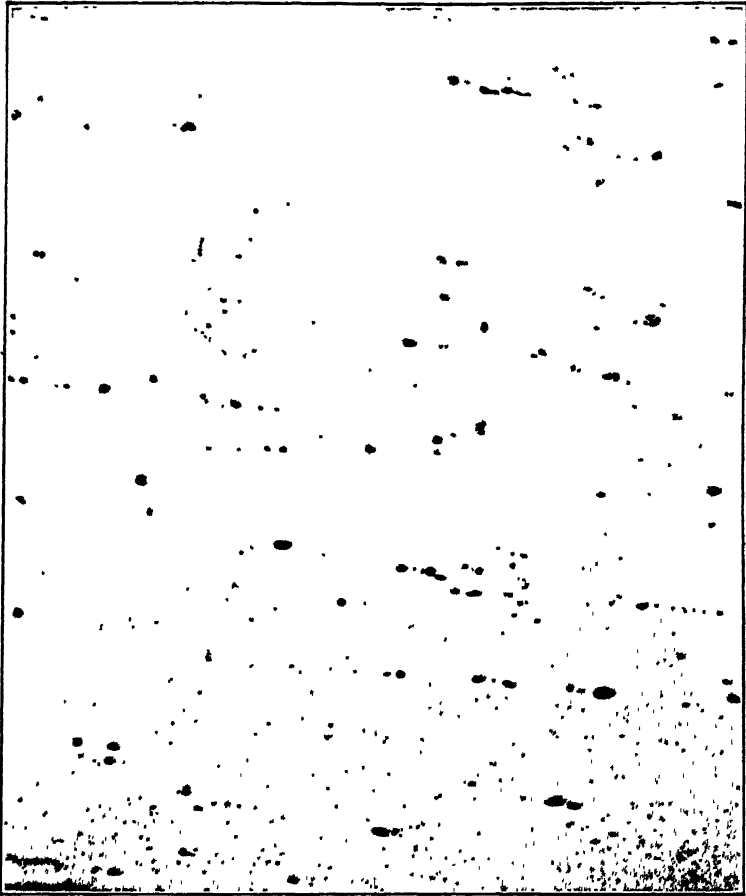


FIG. 34.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF FORGED UNANNEALED BAR. INGOT WAS CAST IN SAND MOLD HAVING AN AREA EQUAL TO AREA OF INGOT.  $\times 20$ .

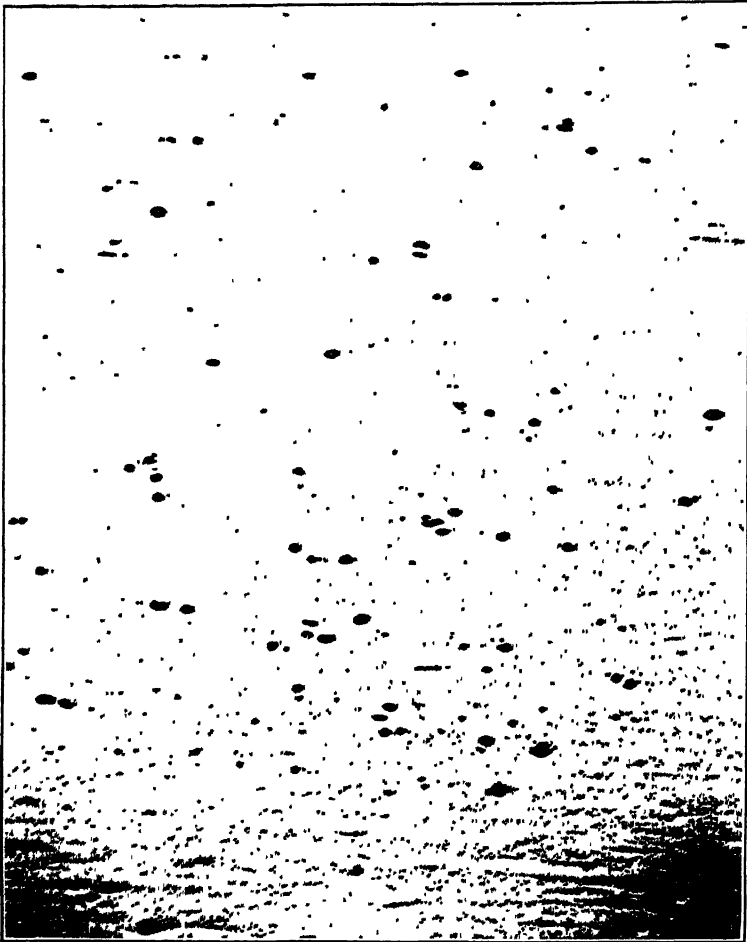


FIG. 35.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF FORGED UNANNEALED BAR. INGOT WAS CAST IN SAND MOLD HAVING AN AREA THREE TIMES AREA OF INGOT.  $\times 20$ .

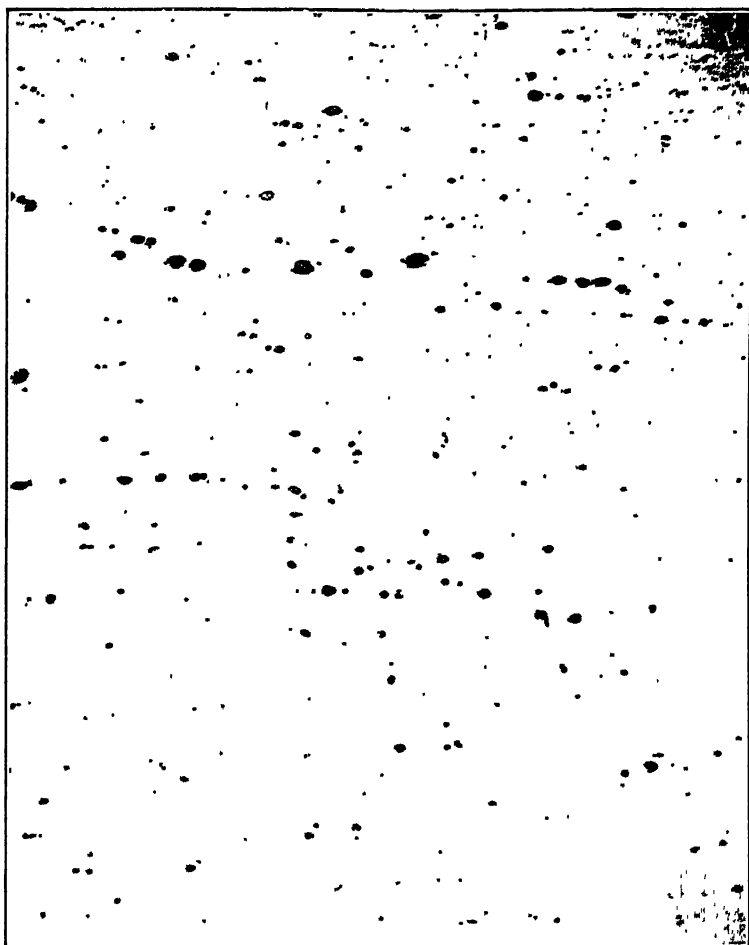


FIG. 36.—UNETCHED LONGITUDINAL SECTION OF LONGITUDINAL TEST BAR TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF FORGED UNANNEALED BAR. INGOT WAS CAST IN SAND MOLD HAVING AN AREA FIVE TIMES AREA OF INGOT.  $\times 20$ .

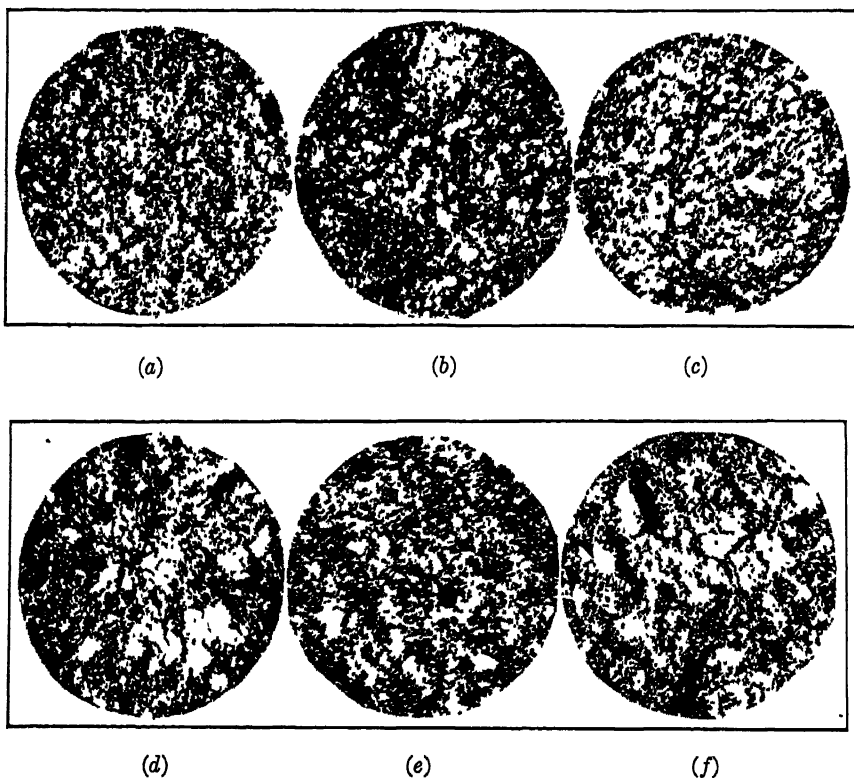


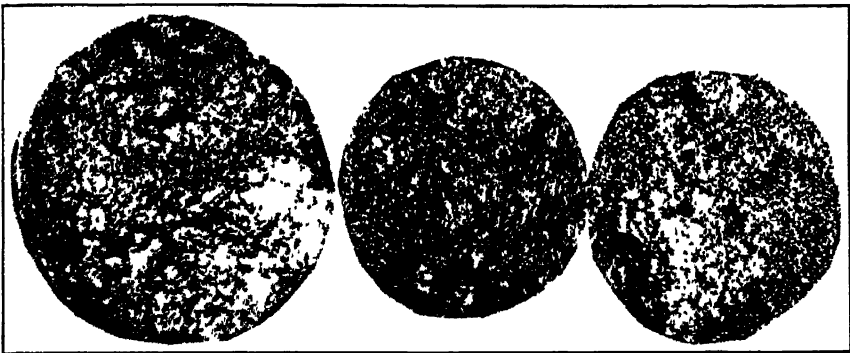
FIG. 37.—GRAIN SIZE OF LONGITUDINAL TEST BARS TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOTS, UNANNEALED. STEEL WAS CAST AS FOLLOWS: (a) IRON-MOLD AREA FIVE TIMES INGOT AREA; (b) IRON-MOLD AREA THREE TIMES INGOT AREA; (c) IRON-MOLD AREA EQUAL TO INGOT AREA; (d) SAND-MOLD AREA EQUAL TO INGOT AREA; (e) SAND-MOLD AREA THREE TIMES INGOT AREA; (f) SAND-MOLD AREA FIVE TIMES INGOT AREA.  $\times 3$ .



(a)

(b)

(c)



(d)

(e)

(f)

FIG. 38.—GRAIN SIZE OF LONGITUDINAL TEST BARS TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF INGOTS, ANNEALED. STEEL WAS CAST AS FOLLOWS: (a) IRON-MOLD AREA FIVE TIMES INGOT AREA; (b) IRON-MOLD AREA THREE TIMES INGOT AREA; (c) IRON-MOLD AREA EQUAL TO INGOT AREA; (d) SAND-MOLD AREA EQUAL TO INGOT AREA; (e) SAND-MOLD AREA THREE TIMES INGOT AREA; (f) SAND-MOLD AREA FIVE TIMES INGOT AREA.  $\times 3$ .



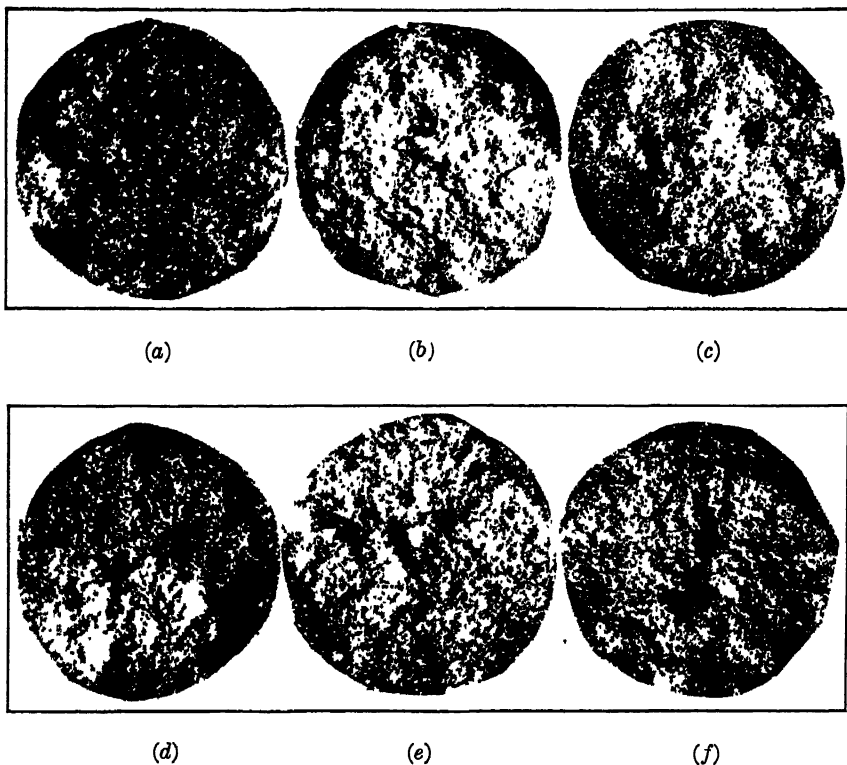


FIG. 39.—GRAIN SIZE OF LONGITUDINAL TEST BARS TAKEN MIDWAY BETWEEN CENTER AND OUTSIDE OF 4-IN. ROUND BARS FORGED FROM 8-IN. INGOT. STEEL WAS CAST AS FOLLOWS: (a) IRON-MOLD AREA FIVE TIMES INGOT AREA; (b) IRON-MOLD AREA THREE TIMES INGOT AREA; (c) IRON-MOLD AREA EQUAL TO INGOT AREA; (d) SAND-MOLD AREA EQUAL TO INGOT AREA; (e) SAND-MOLD AREA THREE TIMES INGOT AREA; (f) SAND-MOLD AREA FIVE TIMES INGOT AREA.  $\times 3$ .

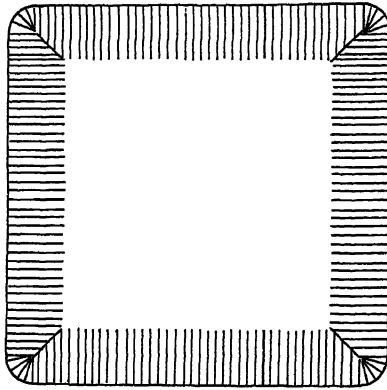


FIG. 40.—LINE OF WEAKNESS FORMED WHERE DENDRITES MEET IN RECTANGULAR INGOTS; CAUSED BY TOO HIGH POURING TEMPERATURE IN MOLDS WITH SHARP CORNERS.

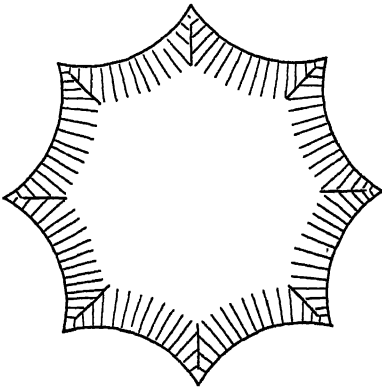


FIG. 41.—LINE OF WEAKNESS FORMED WHERE DENDRITES MEET IN INGOTS WITH SHARP CORRUGATIONS.

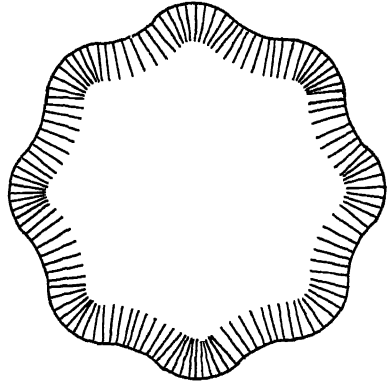


FIG. 42.—NO LINE OF WEAKNESS FORMED IN INGOTS WITH ROUND CORRUGATIONS.

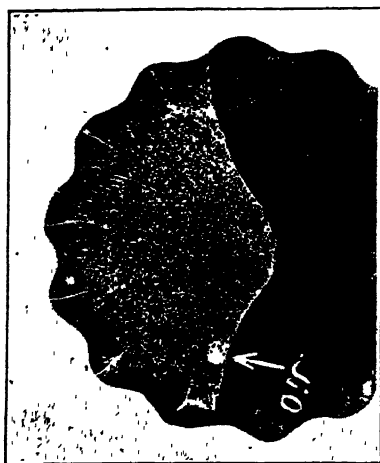


FIG. 43.—INGOT WITH SIXTEEN CORRUGATIONS.

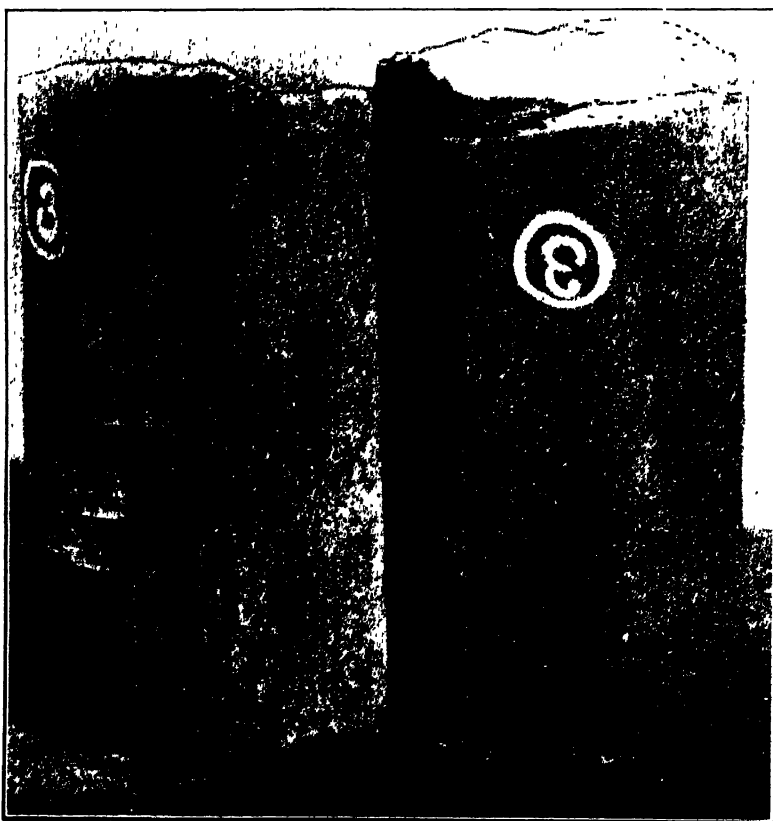


FIG. 44.—LONGITUDINAL TEARS CAUSED BY PARTING IN MOLDS; NOTE FIN OF METAL RUNNING PARALLEL TO CRACKS.



FIG. 45.—FRACTURE SHOWING CROSS-SECTION OF 30-IN. NICKEL-STEEL INGOT; NOTE HOW CRACKS FOLLOW DIRECTION OF DENDRITIC CRYSTALS.

from the head of the metal above it. The crack is more likely to occur on big-end-down ingots, where the ingot contracts and the mold expands leaving the ingot unsupported by the walls of the mold, than in big-end-up ingots because, in the latter, as the ingot contracts and the mold expands the ingot drops into the mold and always has the walls of the mold to support it. Experience has demonstrated, in practice, that the transverse butt cracks may be eliminated by pouring the steel slowly and on the cold side.

Molds are being used with vertical ribs or corrugations, which solidify quickly and strengthen the shell of the ingot so as to withstand the pressure from the ferrostatic head of metal. Cracks frequently occur in the corners of square and rectangular ingots used in rolling mills and alloy-steel plants. These cracks are caused by the segregation of impurities into a plane formed by the junction of dendrites from adjacent mold walls; they are also likely to occur in the highest grade steel if it is poured at too high a temperature. For a long time, many steel men made the error of casting metal at the higher temperatures that could be obtained in the electric furnace. Large radii in the corners of the mold, Fig. 40, would prevent this defect on steel poured at reasonably low temperature.

In the case of round ingots commonly used for forging purposes, the type of corrugation and temperature at which the steel is poured have an important relation with one another. Molds of this type are made with from eight to thirty-two corrugations or flutes. For ordnance work, it was general practice to use an octagon mold with either a sharp- or a round-cornered corrugation, Figs. 41 and 42; the round-cornered corrugations have proved the most satisfactory in the writer's experience, sharp-cornered corrugations are likely to develop weak planes where the dendrites meet; this has been demonstrated by test bars taken from these points. These defects have also been witnessed in the slicing of ingots preparatory to boring for making hollow forgings; in some instances, where the steel was poured on the hot side, small open cracks have been seen with the naked eye.

The type of corrugation that offers the greatest protection against cracks for wide variations in pouring temperature is shown in Fig. 42; the dendrites do not meet and no plane of weakness is formed. An ingot, with sixteen corrugations, where cracks were developed as a result of teeming the metal at too high a temperature, is shown in Fig. 43.

Molds should be designed in such a manner as to relieve the ingot of all undue strains during solidification. In Fig. 44 are shown longitudinal cracks that occurred diametrically opposite one another on the surface of a 30-in. corrugated ingot. Close inspection will show a thin fin of metal running parallel to these cracks; the fin was formed by a parting or opening in the mold and prevented the ingot from contracting freely and set up strains that caused a vertical rupture of the metal. Molds



FIG. 46.—SULFUR PRINT FROM BOTTOM BLOOM OF TOP-CAST INGOT. ONE-HALF ORIGINAL SIZE.



FIG. 47.—SULFUR PRINT FROM TOP BLOOM OF TOP-CAST INGOT. ONE-HALF ORIGINAL SIZE.

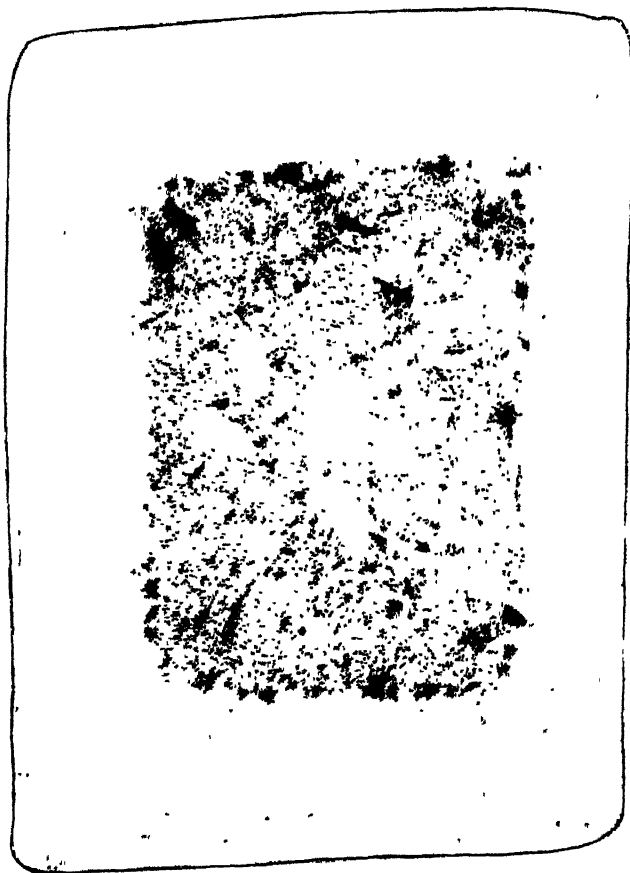


FIG. 48.—SULFUR PRINT FROM BOTTOM BLOOM OF BOTTOM-CAST INGOT. ONE-HALF ORIGINAL SIZE.



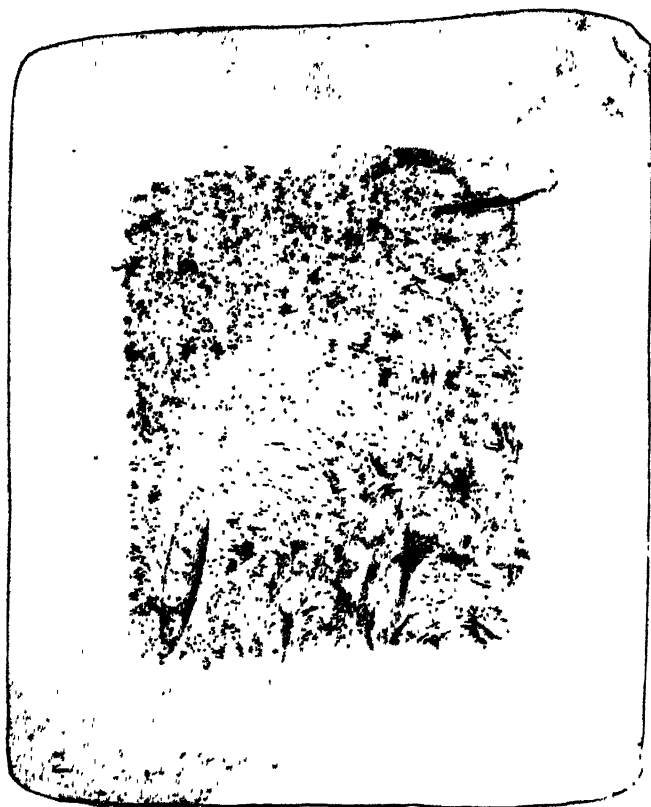


FIG. 49.—SULFUR PRINT FROM TOP BLOOM OF BOTTOM-CAST INGOT. ONE-HALF ORIGINAL SIZE.

should be perfectly smooth and free from indentations that tend to hold the metal and prevent its contracting freely and uniformly. The cross-section of this ingot, with long dendritic crystals on the outer surface, is shown in Fig. 45; it will be noted that these cracks occur in the direction of the dendrites, where the metal is weakest.

#### EFFECT OF METHOD OF POURING

Top pouring is the method most commonly used. The metal may be poured direct from the bottom of the ladle into the mold, or through a tun dish with one or more openings. The tun dish reduces the pressure caused by the head of metal as it comes directly from the ladle; this prevents a certain amount of splash in the mold. The use of a tun dish generally insures a steady stream of metal entering the mold, and corrects, to a certain extent, the bad effects of a leaking nozzle or badly fitted stopper. Tun dishes with several openings reduce the rate of teeming, which results in colder pouring and quicker solidification of the steel. Top pouring gives greater uniformity of composition and structure for deoxidized steel; this, however, is sometimes obtained at the expense of a rough and scabby surface. Top pouring results in less segregation and piping in the case of deoxidized steel; it causes solidification to start as soon as the metal enters the mold. The hot metal poured into the mold from the top continues to fill the shrinkage cavity and prevents pipe from forming; big-end-up molds, for this reason, have a tendency to reduce piping and segregation. Better feeding of the ingot is obtained by decreasing the chill or wall thickness of the mold toward the top. This feeding is still more effective when a hot top of refractory material, or some other form of insulation, is used to maintain a pool of hot metal until the center of the ingot has completely solidified.

Bottom pouring is generally used for ingots requiring a good surface, in the case of both deoxidized and open steel. The additional expense of runners and the scarcity of labor, at the present time, prohibit this method, except where the increased cost is offset by some desired physical property in the ingot that cannot be obtained by top pouring. It is for this reason that steel for die blocks, seamless tubing, and sheets are frequently bottom poured. The metal must be hotter in the ladle for bottom pouring than for top pouring, in order to flow through the runners. To prevent the steel from being cast at this high temperature, which would result in slower cooling, larger grain growth, and greater segregation, the molds are often grouped around a common runner; sometimes as many as twelve to fourteen are cast simultaneously. This results in very slow casting, in some cases as low as  $\frac{1}{4}$  ton per minute, which is advantageous in both deoxidized and open steel, as it results in rapid solidification after casting, thereby giving the finest grain size, less segregation, and less pipe than if the ingots were cast individually.

or in smaller groups. In open steel, slow casting gives thicker-skinned ingots by permitting the gases to pass off, which would otherwise be entrapped and form objectionable blowholes near the surface of the ingot.

Sulfur prints of 8- by 7-in. blooms, rolled from 22- by 22-in. commercial, open-steel ingots, containing 0.14 per cent. carbon, 0.34 per cent. manganese, 0.026 per cent. sulfur, 0.025 per cent. phosphorus on the ladle analysis, are shown in Figs. 46 to 49. These prints illustrate how top pouring prevents segregation at the bottom of the ingot, because of rapid solidification of the metal, while bottom casting at the same temperature promotes it. The casting temperature was about 2850° F. It will be noted that the bottom-cast ingot is segregated from top to bottom, because the hottest metal entered the bottom of the mold at the end of the cast and maintained a liquid center throughout the entire period of pouring. As this same thing occurs in both open and deoxidized steel when bottom cast, it is evident why casting should be done at the slowest possible rate.

#### CONCLUSION

It has been shown in the foregoing that ingotism and segregation, the formation of dendrites, and the distribution of intergranular material bear definite relations to the rate of cooling and solidification of steel in the mold. It has also been shown that steel most rapidly solidified in the mold responds most easily to heat treatment. Forging improves the physical qualities of steel cooled slowly in the mold, but it cannot correct the bad effects resulting from the segregation of intergranular material. While steel should be cast in the mold as cold as possible, in order to obtain uniform structure and chemical analysis, higher temperatures in the furnace before tapping will help rid the steel of occluded gases and foreign non-metallic inclusions and give a better and more uniform solution of alloys and other desirable constituents. The best results are obtained by getting the steel hot in the furnace and making all the additions possible before the steel enters the ladle. In some cases, the steel is cooled in the furnace, but more often it is tapped into the ladle, where it is held until the proper casting temperature is obtained.

#### ACKNOWLEDGMENT

The author desires to express his thanks to the Mesta Machine Co. and its metallurgist, C. I. Niedringhaus, for the facilities and coöperation furnished in making the experimental ingots and performing the test work. Appreciation is also acknowledged to C. E. McQuigg and his staff at the Union Carbide and Carbon Research Laboratories for their assistance in preparing photomicrographs, etc.

## DISCUSSION

EMIL GATHMANN,\* Baltimore, Md. (written discussion).—The author's graphic presentation of his experiments emphasizes the importance of the rate of cooling in determining the type of solidification of ingot structure. For many years, I have considered the rate of cooling of an ingot a fundamental factor in determining the chemical as well as the physical characteristics of the solidified steel casting, and all my ingot and mold designs have been based on this theory.

The numerous macrographs of similar sections of ingots solidified through various rates of cooling and the tables shown should be closely studied by all interested in improvements in the chemical and physical quality of the steel ingot. Specific attention is directed to Table 1, which shows the large variation of carbon segregation in similar ingot sections, solidified under quite different times of cooling.

From the inception of my company's work in ingot and mold design, I have advocated thick heat-absorbing iron mold walls giving a chill ratio of approximately  $2\frac{1}{2}$  to 1 and 3 to 1 at the bottom, or lower portion, of the ingot, usually tapering toward the upper cross-section of the ingot in a 1 to 1 or  $1\frac{1}{4}$  to 1 ratio.

The theory of the solidification of steel ingots, as propounded by Prof. Bradley Stoughton and Dr. Henry Marion Howe in their papers presented before the Institute 1907-08, has been closely followed in my general plans of ingot and mold design for many steel plants, and this theory has been proved to be fundamental.

In my early work in ingot and mold design, the principal objective was the reduction of the shrinkage cavity, or so-called pipe, in the standard big-end-down ingot by means of differential cooling of the ingot, the mold-wall chill gradually decreasing from the bottom to the top of the ingot. In practice with the usual standard big-end-down mold chamber, no material improvement in the ingot structure or reduction of pipe was obtained.

I then advocated the big-end-up chamber, but as great opposition was made to the extended use of the big-end-up mold, because of some necessary changes in administrative practice and fear of reduced tonnage production, we changed the taper or draft of the big-end-down ingot from the normal  $\frac{1}{2}$  in. per ft. to  $\frac{1}{8}$  in. and even to  $\frac{1}{16}$  in. per ft. of ingot body length, thus obtaining substantially parallel chamber walls. In these molds, we used a bottom chill of as much as 6 to 1 with a top ratio approximating 1 to 1, and superimposed or suspended a refractory sink-head, or feeder, at the upper portion of the mold to insure the maintenance of a liquid reservoir of steel until the body of the ingot had solidified. Considerable improvement in ingot structure and reduction of primary pipe were obtained with this design, but secondary piping and excessive

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carbon segregation were invariably found to occur in the mid-vertical section of ingots.

We concluded, more than five years ago, and so advised steelmakers for whom we were designing ingot-mold equipment, that increased ratio of mold chill beyond 2 to 1 was of real value only when employed in conjunction with an ingot of inverted pyramidal form and suitable taper, or of our so-called big-end-up type. It is only in the inverted pyramidal form of ingot-mold chamber that the outer, or peripheral, skin of the ingot remains with the mold walls for any appreciable time, thus allowing uninterrupted absorption or transmission of the heat of the molten solidifying ingot to the mold walls. I have determined from many tests that a taper of  $\frac{1}{4}$  in. per ft. of ingot length is ample when suitable mold chill walls are employed for ingots not exceeding 12 by 12 in. section. For larger ingots, this taper should be increased to approximately  $\frac{1}{2}$  in. for a 25 by 25 in. ingot.

In the big-end-down and uniform-chamber molds, an air gap, or space, forms within a very short time between the outer solidified skin of the ingot and the mold walls, which air gap retards the transmission of heat from the ingot to the mold wall, irrespective of the ratio of chill. In fact, we have found that a very heavy metallic mold wall, when used in conjunction with the big-end-down ingot, actually increases the time of solidification of the interior of the ingot. The only big-end-down molds where heavy walls have any chill influence on the condition of the interior structure of the ingot are those of the fluid compressed type, of which Harmet is the best example. Harmet's mold has a substantially uniform wall thickness giving a chill ratio of approximately 6 to 1; the effect of the chill is increased by water cooling the outer portion of the mold walls. The process was first described in the *Transactions* of the British Iron and Steel Institute in 1902. The Harmet and kindred processes have, however, not been introduced in ingot molding, to any considerable extent, as the required fluid-compression equipment is cumbersome and expensive and not adaptable to tonnage production of quality steel.

That the greater heat absorptive value of heavy, as compared with lighter, metallic or with sand mold walls, favors the important factor of rate of ingot solidification has long been well known to many familiar with the art. As Doctor Howe frequently stated, the shorter the time of solidification, the greater will be the number of independent nuclei from which solidification proceeds. This leads to an increase in the number and in the rapidity of growth of smaller forms of dendrites extending inwardly at right angles from the molded surface, or skin, of the ingot when heavy metallic mold walls chill the ingot. A land-locking type of solidification is thus formed which prevents, or at least retards, free emigration or segregation of non-metallic impurities or matter not in solid solution.

The increase in the number and in the rapidity of growth of the dendrites and decrease in their size is most important, as it prevents, or greatly reduces, coarse crystallization and columnar forms of the outer parts of the ingot, thus building a more homogeneous and stronger ingot structure which is substantially free of clotted segregation. The author has shown that such steel is superior in its response to forging and heat treatment.

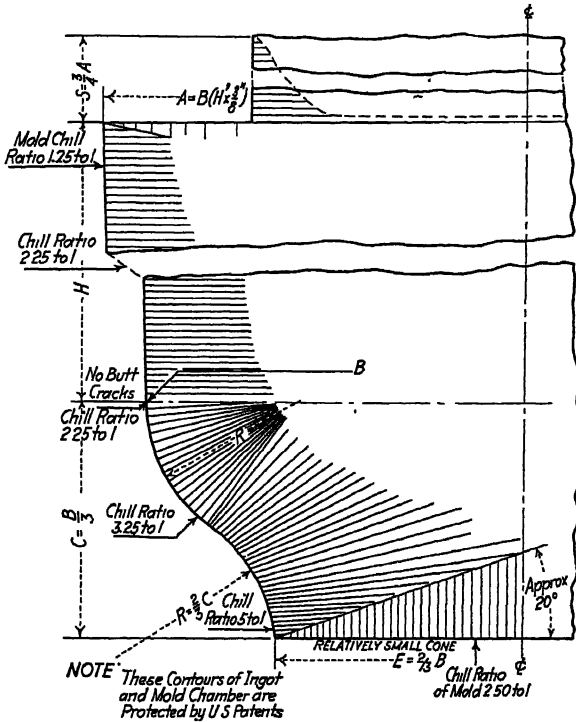


FIG. 50.—VERTICAL SECTION IN BIG-END-UP INGOT.

Fig. 50 illustrates the general contour and relative dimensions of the Gathmann "big-end-up" ingot, the approximate chill ratio of mold being indicated at various ingot sections. About 3,000,000 tons of steel have been produced in this design of mold during the past six years, of which over 1,000,000 tons were made during the year just ended.

Particular attention is called to the bottom contour of compound radii, which prevent the formation of the so-called butt cracks, referred to by the author as being frequently found in vertically tapered or straight-ingot contours. Catches, or binding of the ingot to the mold bottom, are prevented by this bottom contour, which has made possible tonnage production of big-end-up ingots without the necessity of any

extensive changes in plant administration. Several thousand ingots of this contour are cast daily at over twenty steel plants in the United States.

Referring to Figs. 40, 41 and 42, I agree entirely with the author's deductions that the horizontal as well as the vertical contour of ingots should be such that lines of weakness are eliminated or reduced as much as practicable. Although corrugated ingots of suitable design undoubtedly have an outer skin with fewer lines of weakness than the usual rectangular or sharply corrugated ingots, I believe that corruga-

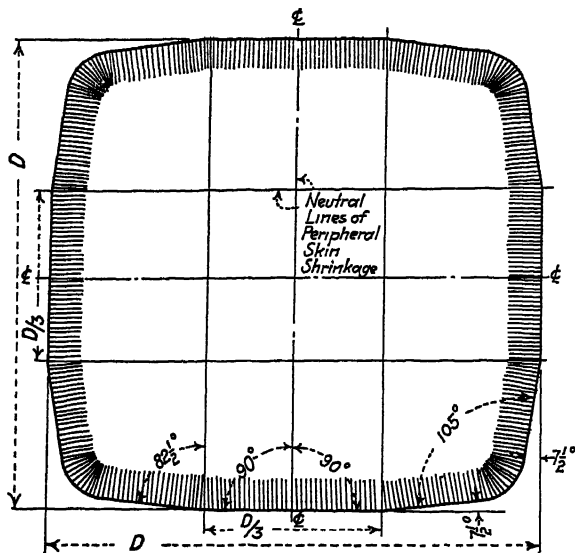


FIG. 51.—HORIZONTAL SECTION OF DIFFERENTIAL CORNER INGOT.

tions or re-entering angles are, in themselves, harmful if they prevent free shrinkage of the ingot without mechanical binding or catches in the mold chamber. By many experiments and much study, I have found that the surface, as well as the interior structure of the ingot, may be considerably improved by giving the mold chamber a definite type of contour whereby a polygonal ingot of substantially rectangular cross-section is formed; this new ingot section is graphically illustrated in Fig. 51. Several steel plants have adopted this type of contour for their mill ingots for quality product, in combination with the vertical contour and mold chill shown in Fig. 50. Approximately 50,000 tons of ingots of this type were rolled last year.

An inspection of Figs. 50 and 51 will show that there is no angular interference of projecting dendrites; hence no lines of weakness or cleavage planes are formed in either the horizontal or the vertical section of the ingot structure, thus fulfilling the requirements set forth by the author in his corrugated ingot structure shown in Fig. 42.

In quality steel, the surface improvement of the differential corner mill ingot has shown saving in chipping costs of approximately 20 per cent. The value of this ingot section in lower grades of steel cast in big-end-down molds has few supporting data, but tests are under way that, I believe, will confirm my deductions that here also considerable surface improvement will be obtained.

Many other fundamentals enter into the tonnage production of improved quality steel than the factor of solidification of the molten steel in the mold. The most important of these may be classified under the headings of "preparation of the molten and suitable finishing of the bath before tapping," "rate of teeming of the molds," "time of stripping," "rate of reheating of the ingot," and "rate of reduction of the ingot." The last named should always be given extreme care, as the ingot, irrespective of its physical condition or chemical analysis, when taken from the soaking pit or heating furnace, is merely a heated steel casting and all the previous care taken to make it sound may be nullified by improper or too rapid working into a forging.

From the supervision, at many steel plants, of the production and working of thousands of ingots of various commercial sizes, I am satisfied that the real value of heavy mold walls or chills can be obtained only when the ingot has a suitable contour of inverted pyramidal form, which is now known in the art as the "big-end-up" type. The ingot should have a contour preventing the formation of lines of weakness and this contour should be such that mechanical hanging or catches between the shrinking, solidifying ingot and the mold chamber walls will not normally occur. The author's experiments prove the correctness of these conclusions.

PAUL E. MCKINNEY,\* Washington, D. C.—Actual observation of work in a number of steel plants has proved that the methods used in solidifying the steel are among the most important factors entering into the production of either steel ingots or castings. Not only are proper methods of solidification necessary for controlling physical characteristics, such as surface of ingot, grain structure, freedom from ingotism, and segregation of the constituents of the steel, but the condition of solidification has a pronounced effect on the purity of the steel and the amount of non-metallic inclusions that will be found in the finished ingot.

It is well known that no matter how well made and how completely refined in the furnace, all steel when it enters the ingot mold will contain some oxygen and gases capable of reacting with the silicon, manganese, and other readily oxidizable constituents of the molten steel. The reaction between these elements continues throughout the solidification period. In the case of long periods of solidification, these inclusions are

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\* U. S. Naval Gun Factory.



formed in copious quantities, freeze out in threads and islands between the dendrites and grains, and, once formed, cannot be removed by forging or heat treatment and must be contended with through all the operations of forging and treating the material. When transverse tests are required, this condition will invariably be productive of test bars with woody structures, or so-called snowflakes, which were such a serious source of difficulty in the production of gun steels during the War. It is safe to state that good steel can be rendered useless by indifferent practice in solidification and that molten steel of questionable quality can be greatly improved by the best practice in solidifying the molten metal.

GEORGE A. DORNIN, Baltimore, Md.—For nearly ten years, my work has been the introduction of ingot molds carrying a heavy mold wall; this experience now covers the making of over 5,000,000 tons of ingots and I agree entirely with the author that rapid chilling of the molten metal in an ingot decreases ingotism and segregation and gives wide, and hence better, distribution of the intergranular material. No advantage is derived from a mold with a chill ratio greater than 3 to 1; I have carefully watched the effect of a chill ratio greater than 3 to 1 in a plant making 1000 tons of high-grade steel a day and could find no benefit from it.

There is one effect of mold chill, however, that the author does not mention and which, in my opinion, is far more important than any other, for if it is neglected actual cavities form in the ingot regardless of what else is done. These cavities are actual voids and, as they are much larger than any aggregate of inclusions can be and as no subsequent heat treatment or forging has any effect on them, they are the most dangerous of steel flaws. They will inevitably be present unless the ingot mold has a differential chill ratio sufficient to cause the dendrites to grow much more rapidly at the bottom of the ingot than at the top.

This growth of dendrites is what governs the successive skin thicknesses, or lines of freezing, of ingots during solidification. These successive skin thicknesses form the boundary walls of the molten interior of the ingot, called by Doctor Howe the "cave," and this cave, if the ingot is to be sound when solid, must be in the shape of an inverted cone or truncated cone, the walls of which must have enough outward flare from bottom to top to prevent bridging. In other words, the converging dendrites must meet each other in the center successively from bottom to top.

In my work, I first tried to attain this condition entirely through mold-wall chill using a big-end-down ingot having the greatest possible chill ratio at its bottom end and the least possible chill ratio at its upper end. Hundreds of thousands of tons of ingots were made in this way before failure was conceded. The effect of mold-wall chill was then combined with the ingot having its big end uppermost and until this combination was worked no really sound steel was made.

The chill ratio is of no benefit when greater than 3 to 1 at the bottom and must be decreased, as we go upward in the mold, to such an extent as to give a combined chill ratio in the mold of between 3 to 1 and 4 to 1; this is necessary to prevent bridging along the axis of the ingot and the consequently inevitable formation of a zone of flaws at this point.

I recently split a forging steel ingot cast in a big-end-down mold of standard dimensions on which a refractory hot top had been used. This ingot weighed approximately three tons, was made from a carefully deoxidized heat of steel, and was poured at the lowest possible temperature; hence it may be regarded as good practice in a big-end-down ingot. It was approximately 20 in. square. Along the axis of this ingot and extending within 10 in. of its bottom end was a flawed zone approximately 5 in. square. This flawed zone, in one plane, contained more than twenty-five flaws varying in length from  $\frac{1}{8}$  to  $\frac{3}{4}$  in. Had this ingot been rolled into bars for forging not 1 per cent. of it would have been sound; yet it is representative of the best that can be gotten with a big-end-down ingot. Heavy mold chills would have had no effect on the location or size of these flaws. Heavy mold-wall chill is of value in the production of sound steel only when it is employed in conjunction with the big-end-up mold and when it is used as an aid in outwardly distorting the lines of freezing of ingots from bottom to top, hence only when used progressively.

## Economic Significance of Metalloids in Basic Pig Iron in Basic Open-hearth Practice

BY C. L. KINNEY, JR., SOUTH CHICAGO, ILL.

(New York Meeting, February, 1924)

THE rapid increase in the amount of steel produced by the basic open-hearth process is an index of its ability to produce high-grade steel from raw materials of the most varied physical character and chemical analysis. This inherent adaptability of the process has resulted in a lack of care in the selection of raw materials, so that in far too many cases charges are used of a chemical and physical character not justified by local economic conditions.

A practice, or series of practices, should be used that will result in the greatest economy for the plant as a whole; therefore, the operations of blast furnace and open hearth must be considered together. In this paper, an effort has been made to show those variations in both open-hearth practice and cost that follow changes in the analysis of the pig iron and it may be said that the theoretical costs shown are worthy of careful study and consideration.

Carbon, manganese, silicon, phosphorus, and sulfur constitute the principal metalloids in basic pig iron and play the leading role in the production of steel by the basic open-hearth process. The percentages of each of these metalloids, with the exception of carbon, is a variable that has its genesis in the economic relation of the blast-furnace plant to its ore and fuel supplies. As the amount of carbon in the iron is a saturation function of the temperature at which it is produced, the variation in the amount carried is, for any given locality and grade of iron, practically negligible and is so considered in the eight heats discussed in this paper.

The melting and refining reactions in an open-hearth furnace, either acid or basic, are essentially oxidizing and vary greatly with the type and age of the furnace, as well as the character of the fuel employed. The outstanding characteristic of the basic process, and the one that explains its predominance over the acid, is its ability to form out of the lime charged and the phosphorus oxidized from the charge a stable

calcium phosphate, which is held in solution by the basic slag. The necessity for such a process had its origin in the gradually diminishing quantities and increasing cost of iron ores having a phosphorus content sufficiently low to permit the production of iron, which contained an amount of this element small enough to make possible its conversion into merchantable steel by the acid process. So the problem is how, and to what degree, the changes in hot metal constitution affect burdening practice, for the open-hearth process is a metallurgical operation that takes various materials and produces steel to meet trade specifications; and the management must meet these chemical and physical specifications in the most economical manner possible.

In this paper, eight representative heats have been chosen and worked out on a chemical, or material, and thermal balance and then combined on a cost basis, in an effort to determine what grouping of materials will yield the lowest cost to the mill as a unit.

The conversion of pig iron into steel requires the elimination, as far as possible, of the silicon, phosphorus, and sulfur and the reduction of carbon. The oxidizing action of the flame with high iron charges must be increased by the introduction of iron oxide in the form of ore, for these metalloids (except carbon) must be oxidized before they can be taken up and held by the slag. The principal slag-forming constituent is lime, and enough must be introduced with the charge to absorb and carry away the impurities. Any excess lime or ore charged is a distinct loss both in heat and material. An excessively thick slag offers an increased resistance to heat transfer from gas to bath, and excess ore produces an overoxidized and soft melting heat, as well as heavy iron losses in the slag.

In our practice, a charge of 35 per cent. metal (carrying 0.75 per cent. silicon, 1.00 per cent. manganese, 0.20 per cent. phosphorus, 4.30 per cent. carbon, and 0.04 per cent. sulfur) together with 65 per cent. scrap will, under average conditions, melt at approximately 0.50 per cent. carbon, which is sufficient when making soft steel to give the active carbon boil so essential for the proper refinement of the charge. As is the case in all large steel-producing districts, the scarcity and price of heavy melting steel scrap make it more economical to substitute the high-percentage-iron charge for the scrap; this substitution necessitates an enhancement of the oxidizing power of the furnace. This is accomplished by charging in the furnace, with the limestone and scrap, a predetermined amount of oxygen in the form of iron ore. The action of the oxygen, thus introduced, on the metalloids in the excess iron charged is a preferential one, at the temperatures prevailing in the furnace at the time the hot iron is poured on the limestone, scrap, and ore previously charged. The silicon, manganese, and phosphorus are first oxidized and, as the temperature rises, the carbon-oxygen reaction begins to

predominate, and on further temperature rise it becomes the only one. It is at this period of the melt, because of the enormous volumes of carbon monoxide and carbon dioxide generated, that the gas-saturated slag occupies two or three times its normal volume; to prevent destructive erosion of the furnace structure, it is customary to run off from 30 to 40 per cent. of this total slag. In spite of the fact that this run-off slag contains relatively high percentages of iron and manganese, in the form of silicates, which if held in the furnace could be more thoroughly reduced and their additional oxygen made available and the metal returned to the bath, the general practice is to waste this slag; and with cheap iron and ores, it is probably more economical to do so than to reduce the size of the charges and to use the additional fuel that the greater finishing slag volume would necessitate.

To illustrate the preceding principles, one scrap and seven ore heats have been calculated on a material and heat-balance basis. The analyses of the various pig irons and the names by which the heats will be herein-after referred to are:

HEAT	PIG-IRON ANALYSIS				
	CARBON, PER CENT.	SILICON, PER CENT.	PHOS- PHORUS, PER CENT.	MANGA- NESE, PER CENT.	SULFUR, PER CENT.
Scrap.....	4.30	0.75	0.20	1.00	0.04
Standard iron.....	4.30	0.75	0.20	1.00	0.04
Standard iron, low-silica ore .	4.30	0.75	0.20	1.00	0.04
High-manganese iron.....	4.30	0.75	0.20	2.00	0.04
High-manganese iron, low- silica ore.....	4.30	0.75	0.20	2.00	0.04
Excess limestone.....	4.30	0.75	0.20	1.00	0.04
High-silicon iron.....	4.30	1.75	0.20	1.00	0.04
High-phosphorus iron.....	4.30	0.75	0.70	1.00	0.04

The scrap charge was 35,000 lb. hot metal and 65,000 lb. heavy scrap; all others were made up of 65,000 lb. hot metal, 35,000 lb. of scrap, and varying amounts of ore. "Low-silica ore" means that the ore carried 4.62 per cent. silica instead of 9.29 per cent. as in the other cases.

It may be properly asked what advantage may be gained or reliance placed on results of heats calculated in this manner; all were calculated using the same factors and, in the cases that correspond to operating conditions in the Chicago district, the theoretical results obtained corresponded very satisfactorily with our actual operation. These typical heats, on a cost basis, showed the following results:

Scrap.....	\$29.11	High-manganese iron, low-silica ore.	\$29.77
Standard iron.....	30.70	Excess limestone.....	31.57
Standard iron, low-silica ore..	30.27	High-silicon iron.....	32.21
High-manganese iron.....	30.27	High-phosphorus iron.....	31.12

TABLE 1.—Comparative Costs of the Different Heats. Based on the Calculated Chemical and Thermal Balance Sheets and Market Prices of April, 1923

Materials Used	Price per Gross Ton			Scrap			Standard Iron High-silica Ore			Standard Iron Low-silica Ore			High-manganese Iron High-silica Ore		
	Tons	Amount	Cost per Ton	Tons	Amount	Cost per Ton	Tons	Amount	Cost per Ton	Tons	Amount	Cost per Ton	Tons	Amount	Cost per Ton
Beds not metal.....	\$ 28.00	15.63			\$ 437.64		29.02	\$ 812.56		29.02	\$ 812.56		20.02	\$ 812.56	
Iron in ferromanganese.....	28.00	0.035			0.98		0.047	1.32		0.040	1.12		0.014	0.39	
Heavy melting steel scrap.....	24.00	29.02			696.43		15.63	375.12		15.63	375.12		15.63	375.12	
Metal from ore.....	12.00						2.12	25.44		2.12	25.44		2.32	27.84	
Pure manganese from 80 per cent. ferro.....	162.50	0.142			23.08		0.189	30.71		0.162	26.33		0.055	8.94	
Gross metallic mixture.....					\$1,158.18	\$28.32		\$1,245.15	\$39.39		\$1,240.57	\$29.14		\$1,224.85	\$28.86
Heavy scrap recovered.....	\$ 24.00	0.446			\$ 10.70		0.467	\$ 11.21		0.467	\$ 11.21		0.409	11.26	
Pit scrap recovered.....	20.00	1.339			26.78		1.403	28.06		1.403	28.06		1.409	28.18	
Net metallic mixture.....					\$1,120.70	\$27.40		\$1,205.88	\$28.47		\$1,201.80	\$28.22		\$1,185.41	\$27.93
Limestone.....	\$ 2.00	1.05			\$ 2.10		2.94	\$ 5.88		2.00	\$ 4.00		3.09	\$ 6.18	
Fluorspar.....	23.00	0.134			3.08		0.134	3.08		0.134	3.08		0.134	3.08	
Calced dolomite.....	9.00	0.446			4.01		1.12	10.08		1.12	10.08		1.12	10.08	
Coal.....	7.00	8.53			59.71		10.43	78.01		9.75	68.25		11.04	77.28	
Slag disposal.....	0.50	1.79			0.90		5.10	\$ 2.55		4.01	2.01		5.34	2.67	
Total.....					\$ 69.80	\$ 1.71		\$ 94.00	\$ 2.23		\$ 87.32	\$ 2.05		\$ 99.20	\$ 2.34
Total cost.....					\$1,190.50			\$1,300.43			\$1,288.62			\$1,284.70	
Cost per ton of ingots.....						\$29.11			\$30.70			\$30.27			\$30.27

TABLE 1.—(Continued)

Materials Used	Price per Gross Ton	High-manganese Iron Low-silica Ore			Excess Limestone			High-silicon Iron			High-phosphorus Iron		
		Tons	Amount	Cost per Ton	Tons	Amount	Cost per Ton	Tons	Amount	Cost per Ton	Tons	Amount	Cost per Ton
Basic hot metal.....	\$ 28.00	29.02	\$ 812.56		29.02	\$ 812.56		29.02	\$ 812.56		29.02	\$ 812.56	
Iron in ferromanganese.....	28.00	0.005	0.14		0.056	1.57		0.006	1.85		0.057	1.60	
Heavy melting steel scrap.....	24.00	15.63	375.12		15.63	375.12		15.63	375.12		15.63	375.12	
Metal from ore.....	12.00	2.32	27.84		2.12	25.44		3.00	36.00		2.56	30.72	
Pure manganese from 80 per cent ferro.....	162.50	0.019	3.09		0.225	36.56		0.263	42.74		0.228	37.05	
Gross metallic mixture.....			\$1,218.75	\$28.54		\$1,251.25	\$29.81		\$1,268.27	\$30.17		\$1,275.05	\$29.56
Heavy scrap recovered.....	\$ 24.00	0.469	\$ 11.26		0.467	\$ 11.21		0.476	\$ 11.42		0.472	\$ 11.33	
Pit scrap recovered.....	20.00	1.409	28.18		1.403	28.06		1.429	28.58		1.416	28.32	
Net metallic mixture.....			\$1,179.31	\$27.62		\$1,211.98	\$28.88		\$1,228.27	\$29.22		\$1,217.40	\$28.03
Limestone.....	\$ 2.00	2.06	\$ 4.12		5.21	\$ 10.42		6.73	\$ 13.46		4.23	\$ 8.46	
Fluorspar.....	23.00	0.134	3.08		0.268	6.16		0.134	3.08		0.134	3.08	
Calined dolomite.....	9.00	1.12	10.08		1.12	10.08		1.12	10.08		1.12	10.08	
Coal.....	7.00	10.33	72.31		11.86	83.02		13.51	94.57		11.60	81.20	
Slag disposal.....	0.50	4.13	2.07		6.90	3.45		9.38	4.69		6.39	3.20	
Total.....			\$ 91.66	\$ 2.15		\$ 113.13	\$ 2.69		\$ 125.88	\$ 2.99		\$ 106.02	\$ 2.49
Total cost.....			\$1,270.97			\$1,325.11			\$1,354.15			\$1,323.42	
Cost per ton of ingots.....				\$29.77			\$31.57			\$32.21			\$31.12

While the scrap heat does not represent regular practice in the South Chicago district, it is included to show what economies might be realized by this simple melting process, when the relative cost of heavy melting scrap and iron permit. The heats with the low-silica ore have been included to show the savings possible from this source. The excess-limestone heat was included to show that this customary method of reducing sulfur is expensive.

As already mentioned, the open-hearth reactions are highly oxidizing, and the oxidizing capacity of the furnace when high percentages of iron are charged must be enhanced by the introduction of an amount of oxygen in the form of iron ore. The demand for ore will depend on the type and age of the furnace and the weight of metalloids charged. The method of determining the amount of ore needed will be explained later.

While the exact constitution of a basic open-hearth slag is not thoroughly understood and analyses vary over wide limits, a good slag will always possess certain outstanding characteristics. Such a slag may be considered to consist of a phosphate and a silicate portion, the former being held in solution by the silicate slag. Moreover the basic and acid constituents must be so proportioned as to permit the slag to hold the impurities, and also to be of the proper consistency at the temperature of the furnace. This physical property might be termed fluidity.

So with a set of factors for determining the amount of ore and lime and the quantity of slag that the charge would yield, the chemical balance sheets for the eight heats were worked out, as well as the thermal balance sheets. Data on how much coal would be required to supply the heat needed to balance the heat generated and heat absorbed were taken from a paper by G. R. McDermott and myself,<sup>1</sup> as well as the general method of calculating the thermal balance sheets.

Using these values for material and coal, as well as product and scrap, a comparative cost sheet was made for the various heats, using market quotations of April, 1923, as the base price, with the results shown in Table 1. It will be noted that the high-manganese iron and low-silica ore heat has a price advantage of \$0.50 a ton over all the other ore heats. Next come the standard-iron low-silica ore and high-manganese iron high-silica ore heats, which are about on a par. The standard-iron high-silica ore heat costs \$0.43 a ton more than the standard-iron low-silica ore, while the excess-limestone, high-silicon iron, and high-phosphorus-iron heats cost from \$0.42 to \$1.51 a ton more than the standard-iron high-silica ore heat.

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<sup>1</sup> The Thermal Efficiency and Heat Balance of an Open-hearth Furnace. *Year Book*, Am. Iron and Steel Inst. (1922) 464.



TABLE 2.—Practice Data of the Different Heats

	Scrap	Standard Iron High-silica Ore	Standard Iron Low-silica Ore	High-manganese Iron High-silica Ore
Per cent. ingots .....	91.62	90.58	91.04	90.39
Per cent. heavy scrap .....	1.00	1.00	1.00	1.00
Per cent. pit scrap .....	3.00	3.00	3.00	3.00
Per cent. loss .....	5.08	5.42	4.96	5.01
Tons of ingots .....	40.90	42.36	42.57	42.44
Hot-metal analysis .....	C, 4.30; Si, 0.75; P, 0.2; Mn, 1.00; S, 0.04	C, 4.30; Si, 0.75; P, 0.2; Mn, 1.00; S, 0.04	C, 4.30; Si, 0.75; P, 0.20; Mn, 1.00; S, 0.04	C, 4.30; Si, 0.75; P, 0.2; Mn, 2.00; S, 0.04
Hot metal, per cent. charged .....	65.00	62.05	62.05	61.79
Scrap, per cent. charged .....	65.00	33.41	33.41	33.27
Iron from ore .....		4.54	4.54	4.63
Silica in ore .....		9.20	4.62	9.29
Pounds coal per ton of ingots .....	497.0	551.0	511.0	583.0
Pounds limestone per ton of ingots .....	57.0	155.00	105.0	193.0
Pounds pure manganese in ladle per ton .....	7.8	10.0	8.5	9.0
Residual manganese in bath .....	0.24	0.20	0.23	0.34
Weight of slag, pounds .....	4,003.0	11,423.0	8,975.0	11,905.0
Weight of iron in slag, pounds .....	536.0	1,728.0	1,274.0	1,432.0

	High-manganese Iron Low-silica Ore	Excess Limestone	High-silicon Iron	High-phosphorus Iron
Per cent. ingots .....	90.92	89.76	88.23	90.11
Per cent. heavy scrap .....	1.00	1.00	1.00	1.00
Per cent. pit scrap .....	3.00	3.00	3.00	3.00
Per cent. loss .....	5.08	6.24	7.77	5.88
Tons of ingots .....	42.70	41.97	42.04	42.53
Hot-metal analysis .....	C, 4.30; Si, 0.75; P, 0.2; Mn, 2.00; S, 0.04	C, 4.30; Si, 0.75; P, 0.2; Mn, 1.00; S, 0.04	C, 4.30; Si, 1.75; P, 0.2; Mn, 1.00; S, 0.04	C, 4.30; Si, 0.75; P, 0.7; Mn, 1.00; S, 0.04
Hot metal, per cent. charged .....	63.27	62.05	60.91	61.48
Scrap, per cent. charged .....	33.79	33.41	32.80	33.10
Iron from ore .....	4.63	4.54	6.29	5.11
Silica in ore .....	4.63	9.20	9.29	9.29
Pounds coal per ton of ingots .....	542.0	633.0	720.0	612.0
Pounds limestone per ton of ingots .....	108.0	278.0	359.0	224.0
Pounds pure manganese in ladle per ton .....	1.0	12.0	14.0	12.0
Residual manganese in bath .....	0.40	15.46	0.12	0.16
Weight of slag, pounds .....	9,254.0	15,466.0	20,897.0	14,318.0
Weight of iron in the slag, pounds .....	940.0	2,536.0	3,624.0	1,918.0

For convenience a condensed cost and practice sheet, which shows some of the salient features of the various heats, and a condensed thermal balance sheet, are given as Tables 3 and 4; the complete ones are given as Tables 5-12.

TABLE 3.—*Combined Practice and Cost Sheet*

Type of Charge	Weight Iron Ore, Pounds	Weight Total Charge, Pounds	Tons of Ingots	Per Cent. Ingots	Residual Mn, Per Cent.	80 Per Cent. FeMn Added, Pounds	Weight of Slag, Pounds	Weight Iron in Slag, Pounds	Weight Mangan- ese in Slag, Pounds	Cost per Ton
Scrap.....	0	100,000	40.90	91.62	0.24	413	4,003	536	219	\$29.11
Standard iron, high-silica ore.....	4,746	104,746	42.36	90.58	0.20	530	11,423	1,728	504	30.70
Standard iron, low-silica ore.....	4,746	104,746	42.67	91.04	0.23	453	8,975	1,274	466	30.27
High-manganese iron, high-silica ore.....	5,183	105,183	42.44	90.39	0.34	153	11,965	1,432	913	30.27
High-manganese iron, low-silica ore.....	5,183	105,183	42.70	90.92	0.40	54	9,254	940	841	29.77
Excess limestone. . .	4,746	104,746	41.97	89.76	0.16	631	15,465	2,536	544	31.57
High-silicon iron.....	6,718	106,718	42.04	88.23	0.12	736	20,897	3,624	589	32.21
High-phosphorus iron.	5,725	105,725	42.53	90.11	0.16	640	14,318	1,918	541	31.12

TABLE 4.—*Condensed Thermal Balance Sheet*

Type of Charge	Heat Absorbed, Millions B.t.u.	Heat Gener- ated, Millions B.t.u.	Heat to be Supplied in Furnace, Millions B.t.u.	At 17.3 Per Cent. Effective Heat to be Supplied in Gas, Millions B.t.u.	At 10,625 B.t.u. per Pound Total Pounds Coal per Heat	Pounds of Coal per Ton of Ingots
Scrap.....	46.84	11.71	35.13	203.06	19,111	467
Standard iron, high-silica ore.....	64.71	21.77	42.94	248.21	23,361	551
Standard iron, low-silica ore.....	62.04	21.43	40.61	232.06	21,841	511
High-manganese iron, high-silica ore.....	68.74	23.27	45.47	262.83	24,737	583
High-manganese iron, low-silica ore.....	65.38	22.85	42.53	245.84	23,137	542
Excess limestone.....	70.67	21.84	48.83	282.25	26,564	633
High-silicon iron.....	85.84	30.20	55.64	321.61	30,269	720
High-phosphorus iron...	74.60	26.77	47.83	276.47	26,021	612

The amount of ore required for a 65 per cent. iron heat depends largely on whether all of the slag is held in the furnace or whether part of it is run off. In the first case, time is allowed for all the earthy bases to work up and convert the iron and manganese silicates into their oxides and basic silicates; then, by the reducing action of the carbon boil, iron and manganese are free to return to the metal bath. The other practice calls for enough ore to convert the manganese and silicon into silicates and the phosphorus into ferrous and ferric phosphate, in which form they are largely removed from the furnace in the run-off slag. The required amounts of ferric oxide in the form of ore for each method are shown in the following table,<sup>2</sup> and are applicable to actual operating conditions. For the sake of simplicity, the costs and thermal and chemical balance sheets shown are based on the first-named practice.

	PER CENT. OF $\text{Fe}_2\text{O}_3$	
	NO RUN-OFF	WITH RUN-OFF
1 per cent. silicon requires . . . . .	4.32	7.62
1 per cent. phosphorus requires . . . . .	4.30	7.80
1 per cent. manganese requires . . . . .	0.97	0.97
1 per cent. carbon requires . . . . .	3.60	4.44

The metalloids in part of the pig iron may be considered to be eliminated by the oxidizing capacity of the furnace, while those belonging to the remaining quantity of pig iron charged determine the ore requirement. In practice, it is found that a scrap heat composed of 65 per cent. light scrap and 35 per cent. pig iron melts at about 0.50 per cent. carbon. This so-called oxidizing power of a furnace is largely measured by the amount of iron oxide, or scale, formed during the melting down of the scrap. With ore heats, this oxidizing action is somewhat less; and for the cases under consideration was considered to be 10 per cent. less than in the scrap heat. So the ferric oxide charged for the standard ore heat will be that required to eliminate the metalloids from 33,000 lb. of pig iron. The requirements for the high-silicon, phosphorus, and manganese iron heats will be the standard ore figure plus the iron oxide needed to eliminate the increased quantity of metalloids charged.

One of the most vital factors in the economical operation of a basic open-hearth furnace is the slag; and on account of improper composition and excessive volumes, the process as a whole suffers very grave losses. While such losses cannot be entirely eliminated, because of lack of ability to forecast accurately the variation in the quantities of acids to be charged, the tendency at all times is to charge an excess of earthy bases to care for the occasional peak of acids. The determination of the quantities of earthy bases to be charged for any given amounts of silica and phosphorus

<sup>2</sup> Carl Dichmann: "The Basic Open-hearth Steel Process." Tr. by Alleyne Reynolds. D. Van Nostrand Co., New York, 1911.

TABLE 5.—Scrap, Furnace Charge  
CHEMICAL BALANCE SHEET

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Material	Weight, in Pounds	Per Cent. C	Pounds C	Pounds CO	Per Cent. Si	Pounds Si	Per Cent. SiO <sub>2</sub>	Pounds SiO <sub>2</sub>	Per Cent. P	Pounds P	Per Cent. P <sub>2</sub> O <sub>5</sub>	Pounds P <sub>2</sub> O <sub>5</sub>	Per Cent. Mn	Per Cent. MnO	Pounds Mn	Per Cent. S
Basic hot metal.....	35,000	4.30	1,505		0.75	263		562	0.20	70		160	1.00		350	0.04
Structural steel scrap.....	65,000	0.20	130						0.01	7		16	0.40		260	0.04
Open-hearth steel.....																
Manganese (natural).....	2,343						0.34	8	0.006							
Indigenous limestone.....	1,000						1.32	13	0.004							
Crushed dolomite.....	1,300						1.12	8	0.004							0.042
Fluorspar.....																0.126
SiO <sub>2</sub> from furnace structure.....								100								
Total entering furnace.....			1,635			263		686	0.01	77		176	0.24		610	0.04
Total steel in bath.....	96,616	0.20	193							10					232	
Tapping slag, 99.04 per cent.....	4,003		193				17.15	685		67	3.83	163	7.07		219	0.25
Total output.....								686		77					451	
Unaccounted for.....															-159	
Metalloids oxidized.....			1,442			263				67					378	

Material	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
Material	Pounds S	Per Cent. CaO	Pounds CaO	Per Cent. MgO	Pounds MgO	Per Cent. Fe	Pounds Fe	Per Cent. FeO	Pounds FeO	Per Cent. Fe <sub>2</sub> O <sub>3</sub>	Pounds Fe <sub>2</sub> O <sub>3</sub>	Per Cent. Al <sub>2</sub> O <sub>3</sub>	Pounds Al <sub>2</sub> O <sub>3</sub>	Per Cent. CaF <sub>2</sub>	Per Cent. Vol.	Per Cent. Moist- ure
Basic hot metal.....	14						32,239									
Structural steel scrap.....	26						64,583									
Open-hearth steel.....																
Manganese (natural).....	1	54.60	1,279	0.88	21	0.20	5					0.30	7			1.5
Crushed dolomite.....	1	48.58	496	32.58	326	0.38	4					1.49	11		15.54	
Fluorspar.....												ReO <sub>3</sub>				
SiO <sub>2</sub> from furnace structure.....		2.50	8	0.38	1							1.16	3	92.53		
Total entering furnace.....			1,773		348	99.51	96,898						21			
Total steel in bath.....	42						90,142									
Tapping slag 99.04 per cent.....	39															
Total output.....	10	44.29	1,773	8.67	348		5.36					0.52	21			
Unaccounted for.....	49		1,773		348		96,678		691				21			
Metalloids oxidized.....	+7				348		-150									





TABLE 6.—Continued

## THERMAL BALANCE SHEET

## HEAT ABSORBED

## THERMOCHEMICAL CHANGES

Reduction of oxides of iron  
Heat of formation of  $\text{Fe}_2\text{O}_3 = 3240$  B.t.u.  
Heat of formation of  $\text{FeO} = 2430$

Input  
 $\text{Fe}_2\text{O}_3 = 6,661$        $\text{FeO} = 108$   
Heat of formation  
 $\text{Fe}_2\text{O}_3 = 6661 \times 3240 = 21.58 \times 10^6$   
 $\text{FeO} = 108 \times 2430 = 0.26 \times 10^6$

Total =  $21.84 \times 10^6$

Output  
Tapping slag =  $\text{FeO} = 2229 \times 2430 = 5.42 \times 10^6$

Moisture in ore = 9170  
Total weight of ore = 9170  
Per cent. moisture = 8  
Total water = 734  
Total heat to make steam at  $212^\circ = 734 \times 1092 = 0.80 \times 10^6$   
Specific heat of steam =  $0.42 + 0.00013 \times (2800 + 212) = 0.81$   
Heat in superheat =  $734 \times (2800 - 212) \times 0.81 = 1.54 \times 10^6$   
Total =  $2.34 \times 10^6$

Decomposition of limestone  
Heat of formation  $\text{CaCO}_3$  per lb. = 772 B.t.u.  
Total limestone = 6584  
Total heat required =  $772 \times 6584 = 5.08 \times 10^6$

Moisture 1.5 per cent. = 99  
Total heat to make steam =  $99 \times 1092 = 0.11 \times 10^6$   
Heat in superheat =  $2096 \times 99 = 0.21 \times 10^6$

Total =  $0.32 \times 10^6$

## HEAT GENERATED

Oxidation of carbon, weight = 2667 lb.  
Heat of formation of CO from C per lb. = 4374 B.t.u.  
Heat generated =  $4374 \times 2667 = 11.67 \times 10^6$   
Oxidation of manganese, weight = 604 lb.  
Heat of formation of  $\text{MnO} = 2984$  B.t.u.  
Heat generated =  $2,984 \times 604 = 1.80 \times 10^6$   
Oxidation of silicon, weight = 488 lb.  
Heat of formation of  $\text{SiO}_2 = 11,693$  B.t.u.

Decomposition of improperly burned dolomite  
Total weight of dolomite = 2500 lb.  
Volatile = 15.54 per cent. = 389 lb.  
Assumed 98 per cent = 381 exists as  $\text{CO}_2$   
To drive off  $\text{CO}_2 = 1756$  B.t.u. per lb.  
Total heat to drive off  $\text{CO}_2 = 1756 \times 381 = 0.67 \times 10^6$

## THERMOPHYSICAL CHANGE

Hot metal = 65,000 lb. Temperature =  $2474^\circ$  F.  
Tapping temperature =  $3080^\circ$  F. includes emissivity factor  
Temperature rise ( $3080^\circ - 2474^\circ$ ) =  $606^\circ$  F.  
Specific heat = 0.2

Heat absorbed =  $65,000 \times 606 \times 0.2 = 7.88 \times 10^6$

Scrap = 35,000 lb. Temperature =  $62^\circ$  F.  
Melting temperature scrap =  $2795^\circ$  F.  
Heat required to bring to melting temperature =  $35,000 \times 2,733 \times 0.16 = 15.80 \times 10^6$   
Latent heat of fusion = 72 B.t.u.  
Total heat of fusion =  $35,000 \times 72 = 2.52 \times 10^6$

Heat to raise to temperature of bath = ( $3080 - 2795$ )  $35,000 \times 0.2 = 2.00 \times 10^6$   
Total heat =  $19.82 \times 10^6$

Total heat in molten slag  
Heat in tapping slag =  $11,423 \times 1086 = 12.18 \times 10^6$  B.t.u.  
Total heat absorbed =  $64.71 \times 10^6$  B.t.u.

## AUTHORITIES FOR CONSTANTS USED

## THERMOCHEMICAL CHANGES

Iron oxide reduction—Richards  
Decomposition of limestone—U. S. Bur. of Standards  
Oxidation of C, Mn, Si, P—Richards, LeChatelier, Berthelot, Thomson  
Formation of slag, calculated using Richards' values

## THERMOPHYSICAL CHANGES

Specific heat, pig iron—0.1665—Oberholfer  
Specific heat, soft steel—0.16—Menthur  
Latent heat of fusion, pig iron—Hutter  
Latent heat of fusion, steel—average value—Jetter, Richards, Brisker  
Heat in molten slag—Springorum

## THERMAL BALANCE SHEET

## HEAT ABSORBED

Red. of oxides of Fe =  $16.42$   
Absorp. moist. of ore =  $2.34$   
Decomp. of limestone =  $5.08$   
Absorp. moist. of limestone =  $0.32$   
Decomp. of dolomite =  $0.67$   
Heat in molten slag =  $12.18$   
Heat added to mixer metal =  $7.88$   
Heat added to scrap =  $19.82$

## HEAT GENERATED

Oxidation of C =  $11.67 \times 10^6$   
Oxidation of Mn =  $1.80 \times 10^6$   
Oxidation of Si =  $5.71 \times 10^6$

Oxidation of Si =  $5.71 \times 10^6$   
Oxidation of P =  $1.40 \times 10^6$   
Heat form. slag =  $1.19 \times 10^6$   
Balance heat to be supplied by combustion of gases in furnace =  $42.94 \times 10^6$   
Total B.t.u. =  $64.71 \times 10^6$

## THERMAL EFFICIENCY OF BATH

Thermal efficiency of furnace = 17.8 per cent.  
B.t.u. in gas per pound of coal = 10,625  
Total B.t.u. to be supplied in producer gas =  $42.94 \times 10^6 = 248.21 \times 10^6$  B.t.u.  
0.173  
Total coal burned = 23,361 lb.





TABLE 7.—Continued

## THERMAL BALANCE SHEET

## HEAT ABSORBED

## THERMOCHEMICAL CHANGES

Reduction of oxides of iron	
Heat of formation of $\text{Fe}_2\text{O}_3$ = 3240 B.t.u.	
Heat of formation of $\text{FeO}$ = 2430	
Input	
$\text{Fe}_2\text{O}_3$ = 6781	$\text{FeO}$ = 100
Heat of formation	
$\text{Fe}_2\text{O}_3$ = $3240 \times 6781 = 21.97 \times 10^6$	
$\text{FeO}$ = $2430 \times 100 = 0.24 \times 10^6$	
Total	$22.21 \times 10^6$
Output	
Tapping slag = $\text{FeO} = 1644 \times 2430 = 3.99 \times 10^6$	
Moisture in ore	
Total weight of ore = 8462 lb.	
Per cent. = 8.20	
Total water = 694	
Total heat to make steam at $212^\circ$	
$694 \times 1092 = 0.76 \times 10^6$	
Specific heat of steam = $0.42 + 0.00013 \times (2800 + 212) = 0.81$	
Heat in superheat = $694 \times (2800 - 212) 0.81 = 1.45 \times 10^6$	
Total = $2.21 \times 10^6$	
Decomposition of limestone	
Heat of formation $\text{CaCO}_3$ per lb. = 772 B.t.u.	
Total limestone = 4478	
Total heat required = $772 \times 4478 = 3.46 \times 10^6$	
Moisture 1.5 per cent. = 87	
Total heat to make steam =	
$87 \times 1,092 = 0.07 \times 10^6$	
Heat in superheat = $2,096 \times 87 = 0.14 \times 10^6$	
Total = $3.67 \times 10^6$	

## Decomposition of improperly burned dolomite

Total weight of dolomite = 2500 lb.  
 Volatile = 15.54 per cent. = 389 lb.  
 Assumed 98 per cent. 389 = 381 exists as  $\text{CO}_2$   
 To drive off  $\text{CO}_2$  = 1756 B.t.u. per lb.  
 Total heat to drive off  $\text{CO}_2$  =  $1756 \times 381 = 0.671$

## THERMOPHYSICAL CHANGE

Hot metal = 65,000 lb. Temperature =  $2474^\circ \text{F}$ .  
 Tapping temperature =  $3080^\circ \text{F}$ . includes emissivity factor  
 Temperature rise ( $3080 - 2474$ ) =  $606^\circ \text{F}$ .  
 Specific heat = 0.2  
 Heat absorbed =  $65,000 \times 606 \times 0.2 = 7.88 \times 10^6$   
 Scrap = 35,000 lb. Temperature =  $62^\circ \text{F}$ .  
 Melting temperature scrap =  $2795^\circ \text{F}$ .  
 Heat required to bring to melting temperature =  $2733 \times 35,000 \times 0.16 = 15.30 \times 10^6$   
 Latent heat of fusion = 72 B.t.u.  
 Total heat of fusion =  $35,000 \times 72 = 2.52 \times 10^6$   
 Heat to raise to temperature of bath  $35,000 \times 285 \times 0.2 = 2.00 \times 10^6$   
 Total heat =  $19.82 \times 10^6$   
 Total heat in molten slag  
 Heat in tapping slag =  $8975 \times 1066 = 9.57 \times 10^6$  B.t.u.  
 Total heat absorbed =  $62.04 \times 10^6$  B.t.u.

## HEAT GENERATED

Oxidation of carbon, weight = 2666 lb.	Heat generated = $11,693 \times 488 = 5.71 \times 10^6$
Heat of formation of CO from C per lb = 4374 B.t.u.	Oxidation of phosphorus, weight = 125 lb.
Heat generated = $4374 \times 2666 = 11.66 \times 10^6$	Heat of formation of $\text{P}_2\text{O}_5$ = 10,825 B.t.u.
Oxidation of manganese, weight = 566 lb.	Heat generated = $10,825 \times 125 = 1.35 \times 10^6$
Heat of formation of $\text{MnO}$ = 2984 B.t.u.	Heat of formation of slag, weight = 8975 lb.
Heat generated = $2984 \times 566 = 1.69 \times 10^6$	Heat of formation of slag = 114 B.t.u.
Oxidation of silicon, weight = 488 lb.	Heat generated = $8975 \times 114 = 1.02 \times 10^6$
Heat of formation of $\text{SiO}_2$ = 11,693 B.t.u.	Total heat generated = $21.43 \times 10^6$

## AUTHORITIES FOR CONSTANTS USED

## THERMOCHEMICAL CHANGES

Iron oxide reduction—Richards  
 Decomposition of limestone—U. S. Bur. of Standards  
 Oxidation of C, Mn, Si, P—Richards, LeChatelier, Berthelot, Thomson  
 Formation of slag, calculated using Richards' values

## THERMOPHYSICAL CHANGES

Specific heat, pig iron—0.1665—Oberhoffer  
 Specific heat, soft steel—0.16—Meuthner  
 Latent heat of fusion, pig iron—Hutner  
 Latent heat of fusion, steel—average value—  
 Jetner, Richards, Brisker  
 Heat in molten slag—Springorum

## THERMAL BALANCE SHEET

## HEAT ABSORBED

Red. of oxides of Fe	= 18.22
Absorp. moist. of ore	= 2.31
Decomp. of limestone	= 3.46
Absorp. moist. of limestone	= 0.21
Decomp. of dolomite	= 0.67
Heat in molten slag	= 9.57
Heat added to mixer metal	= 7.88
Heat added to scrap	= 19.82

## HEAT GENERATED

Oxidation of C	= $11.66 \times 10^6$
Oxidation of Mn	= $1.69 \times 10^6$

Oxidation of Si	= $5.71 \times 10^6$
Oxidation of P	= $1.35 \times 10^6$
Heat form. slag	= $1.02 \times 10^6$
Balance heat to be supplied by combustion of gases in furnace	= $40.61 \times 10^6$
Total B.t.u.	= $62.04 \times 10^6$

## THERMAL EFFICIENCY OF BATH

Thermal efficiency of furnace = 17.3 per cent.  
 B.t.u. in gas per pound of coal = 10,625  
 Total B.t.u. to be supplied in producer gas =  $40.61 \times 10^6 = 232.06 \times 10^6$  B.t.u.  
 0.175  
 Total coal burned = 21,841

TABLE 8.—*High-manganese Iron, High-silica Ore, Furnace Charge*

## CHEMICAL BALANCE SHEET

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Material	Weight, in Pounds	Per Cent.	Pounds C	Pounds CO	Per Cent. Si	Pounds Si	Per Cent. SiO <sub>2</sub>	Pounds SiO <sub>2</sub>	Per Cent. P	Pounds P	Per Cent. P <sub>2</sub> O <sub>5</sub>	Pounds P <sub>2</sub> O <sub>5</sub>	Per Cent. Mn	Per Cent. MnO	Pounds Mn	Per Cent. S
Basic hot metal.....	65,000	4.30	2,795		0.75	488		1,089	0.20	130			2.00		1,200	0.04
Structural steel scrap.....	35,000	0.20	70					931	0.01	4			0.40		140	0.04
Chapin ore (natural).....	10,023						9.29	931	0.05	5			0.13		18	
Michigan limestone.....	6,915						0.34	24	0.006							
Calculated dolomite.....	2,500						1.32	33	0.004							0.042
Fluorspar.....	300						1.12	3	0.004							0.126
SiO <sub>2</sub> from furnace structure.....								100								
Total entering fur- nace.....						488										
Total steel in bath.....	99,289	0.20	2,885			488		2,130	0.01	189			0.34		1,453	0.085
Tapping slag, 99.30			199							10					388	
Total output.....	11,965							2,130		129	2.47	290		9.84	913	0.25
Unaccounted for.....						488		2,130		189					1,251	
Metalloids oxidised.....			2,663							129					1,115	

	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
Material	Pounds S	Per Cent. CaO	Pounds CaO	Per Cent. MgO	Pounds MgO	Per Cent. Fe	Pounds Fe	Per Cent. FeO	Pounds FeO	Per Cent. Fe <sub>2</sub> O <sub>3</sub>	Pounds Fe <sub>2</sub> O <sub>3</sub>	Per Cent. Al <sub>2</sub> O <sub>3</sub>	Pounds Al <sub>2</sub> O <sub>3</sub>	Per Cent. CaF <sub>2</sub>	Per Cent. Vol- ume	Per Cent. Mol- ture
Basic hot metal.....	26						60,261									
Structural steel scrap.....	14	1.60	100	2.64	265	51.76	34,772	1.18	118		7,281	1.10	110		3.15	8.00
Michigan limestone.....	3	54.60	2,776	0.88	61	0.20	5,188					0.30	21			
Calculated dolomite.....	3	48.28	1,215	32.58	815	0.38	10					1.49	37		15.54	1.50
Fluorspar.....		2.50	8	0.38	1							1.15	3			
SiO <sub>2</sub> from furnace structure.....																
Total entering furnace.....	46		5,159	1,142	1,142	99.42	100,245						171			
Total steel in bath.....	35						98,718									
Tapping slag, 99.89																
Total output.....	30	43.12	5,159	9.54	1,142		1,432	15.44	1,847		1.43		171			
Unaccounted for.....	65		5,159	1,142	1,142		100,145		1,847				171			
Metalloids oxidised.....	+19						—100		1,847							

TABLE 8.—Continued

## THERMAL BALANCE SHEET

## HEAT ABSORBED

## THERMOCHEMICAL CHANGES

Reduction of oxides of iron	
Heat of formation of $\text{Fe}_2\text{O}_3$ = 3240	
Heat of formation of $\text{FeO}$ = 2430	
Input	
$\text{Fe}_2\text{O}_3$ = 7281	$\text{FeO}$ = 118
Heat of formation	
$\text{Fe}_2\text{O}_3$ = 7281 $\times$ 3240 = 23 59 $\times 10^6$	
$\text{FeO}$ = 118 $\times$ 2430 = 0 29 $\times 10^6$	
Total =	23 88 $\times 10^6$
Output	
Tapping slag— $\text{FeO}$ = 1847 $\times$ 2430 =	
	4 49 $\times 10^6$
Moisture in ore	
Total weight of ore = 10,023	
Per cent. moisture = 8	
Total water = 802	
Total heat to make steam at 212°	
802 $\times$ 1092 = 088 $\times 10^6$	
Specific heat of steam = 0.42 + 0.00013 $\times$	
(2800 + 212) = 0.81	
Heat in superheat 802 $\times$ (2800 - 212) 0.81 =	
1.68 $\times 10^6$	
Total = 2 56 $\times 10^6$	
Decomposition of limestone	
Heat of formation $\text{CaCO}_3$ per lb. = 772 B.t.u.	
Total limestone = 6915	
Total heat required = 6915 $\times$ 772 =	
	5.34 $\times 10^6$
Moisture 1.5 per cent. = 104	
Total heat to make steam =	
104 $\times$ 1092 =	0.11 $\times 10^6$
Heat in superheat = 104 $\times$ 2096 = 0.22 $\times 10^6$	
Total =	0 33 $\times 10^6$

## Decomposition of improperly burned dolomite

Total weight of dolomite = 2500 lb.  
 Volatile = 15.54 per cent = 389 lb.  
 Assumed 98 per cent. = 381 exists as  $\text{CO}_2$   
 To drive off  $\text{CO}_2$  = 1756 B.t.u. per lb.  
 Total heat to drive off  $\text{CO}_2$  = 1756  $\times$  381 =  
 0 67  $\times 10^6$

## THERMOPHYSICAL CHANGE

Hot metal = 65,000 lb. Temperature = 2474° F.  
 Tapping temperature = 3080° F. Includes  
 emissivity factor  
 Temperature rise (3080 - 2474) = 606° F.  
 Specific heat = 0.2  
 Heat absorbed = 65,000  $\times$  606  $\times$  0.2 =  
 7.88  $\times 10^6$   
 Scrap = 35,000 lb. Temperature = 62° F.  
 Melting temperature scrap = 2795° F.  
 Heat required to bring to melting temperature =  
 35,000  $\times$  2733  $\times$  0.16 = 15.30  $\times 10^6$   
 Latent heat of fusion = 72 B.t.u.  
 Total heat of fusion = 35,000  $\times$  72 =  
 2.52  $\times 10^6$   
 Heat to raise to temperature of bath = (3080 -  
 2795) 35,000  $\times$  0.2 = 2.00  $\times 10^6$   
 Total heat = 19.32  $\times 10^6$   
 Total heat in molten slag  
 Heat in tapping slag = 11,965  $\times$  1066 =  
 12.75  $\times 10^6$  B.t.u.  
 Total heat absorbed = 68.74  $\times 10^6$  B.t.u.

## HEAT GENERATED

Oxidation of carbon, weight = 2666 lb.	
Heat of formation of CO from C per lb. =	
4374 B.t.u.	
Heat generated = 4374 $\times$ 2667 =	
	11.66 $\times 10^6$
Oxidation of manganese, weight = 1115 lb.	
Heat of formation of $\text{MnO}$ = 2984 B.t.u.	
Heat generated = 2984 $\times$ 1115 =	
	3 33 $\times 10^6$
Oxidation of silicon, weight = 488 lb.	
Heat of formation of $\text{SiO}_2$ = 11,693 B.t.u.	
Heat generated = 11,693 $\times$ 488 =	
	5.71 $\times 10^6$
Oxidation of phosphorus, weight = 129 lb.	
Heat of formation of $\text{P}_2\text{O}_5$ = 10,825 B.t.u.	
Heat generated = 10,825 $\times$ 129 =	
	1.40 $\times 10^6$
Heat of formation of slag, weight = 11,965 lb.	
Heat of formation of slag = 98 B.t.u.	
Heat generated = 98 $\times$ 11,965 = 1.17 $\times 10^6$	
Total heat generated = 23 27 $\times 10^6$ B.t.u.	

## AUTHORITIES FOR CONSTANTS USED

## THERMOCHEMICAL CHANGES

Iron oxide reduction—Richards  
 Decomposition of limestone—U. S. Bur. of  
 Standards  
 Oxidation of C, Mn, Si, P—Richards, LeChatelier  
 Berthelot, Thomson  
 Formation of slag, calculated using Richards'  
 values

## THERMOPHYSICAL CHANGES

Specific heat, pig iron—0.1665—Oberhoffer  
 Specific heat, soft steel—0.16—Meuthner  
 Latent heat of fusion, pig iron—Hutter  
 Latent heat of fusion, steel—average value—  
 Jetner, Richards, Brisker  
 Heat in molten slag—Springorum

## THERMAL BALANCE SHEET

## HEAT ABSORBED

Red. of oxides of Fe	= 19.89
Absorp. moist. of ore	= 2.56
Decomp. of limestones	= 5.34
Absorp. moist. of limestone	= 0.23
Decomp. of dolomite	= 0.67
Heat in molten slag	= 12.76
Heat added to mixer metal	= 7.88
Heat added to scrap	= 19.32

## HEAT GENERATED

Oxidation of C	= 11.66 $\times 10^6$
Oxidation of Mn	= 3.33 $\times 10^6$
Oxidation of Si	= 5.71 $\times 10^6$

Oxidation of P = 1.40

Heat form. slag = 1.17

Balance heat to be supplied by combustion of  
 gases in furnace = 45.47  $\times 10^6$   
 Total B.t.u. = 68.74  $\times 10^6$

## THERMAL EFFICIENCY OF BATH

Thermal efficiency of furnace = 17.3 per cent.  
 B.t.u. in gas per pound of coal = 10,685  
 Total B.t.u. to be supplied in producer gas =  
 45.47  $\times 10^6$   
 0 173  
 Total coal burned = 24,737 lb



TABLE 9.—*Continued*

## THERMAL BALANCE SHEET

## HEAT ABSORBED

## THERMOCHEMICAL CHANGES

Reduction of oxides of iron	
Heat of formation of $\text{Fe}_2\text{O}_3$ = 3240	
Heat of formation of $\text{FeO}$ = 2430	
Input	
$\text{Fe}_2\text{O}_3$ = 7291	$\text{FeO}$ = 109
Heat of formation	
$\text{Fe}_2\text{O}_3$ = $729 \times 3240 = 23.62 \times 10^6$	
$\text{FeO}$ = $109 \times 2430 = 0.26 \times 10^6$	

Total =  $23.88 \times 10^6$

## Output

Tapping slag  $\text{FeO}$  =  $1213 \times 2430 = 295 \times 10^6$

## Moisture in ore

Total weight of ore = 9250  
 Per cent. moisture = 8.20  
 Total water =  $9250 \times 0.082 = 759$   
 Total heat to make steam at  $212^\circ = 759 \times 1092 = 0.83 \times 10^6$   
 Specific heat of steam =  $0.42 + 0.00013 \times (2800 + 212) = 0.81$   
 Heat in superheat =  $759 \times (2800 - 212) \times 0.81 = 1.59 \times 10^6$

Total =  $2.42 \times 10^6$

## Decomposition of limestones

Heat of formation  $\text{CaCO}_3$  per lb. = 772 B.t.u.  
 Total limestone = 4620  
 Total heat required =  $4620 \times 772 = 3.57 \times 10^6$

Moisture 1.5 per cent. =  $4620 \times 0.015 = 69.3$

Total heat to make steam =  $69.3 \times 1092 = 0.08 \times 10^6$

Heat in superheat =  $69.3 \times 2096 = 0.15 \times 10^6$

Total =  $0.23 \times 10^6$

## [HEAT GENERATED

Oxidation of carbon, weight = 2665 lb.  
 Heat of formation of CO from C per lb. = 4374 B.t.u.  
 Heat generated =  $4374 \times 2665 = 11.66 \times 10^6$

Oxidation of manganese, weight = 1047 lb.  
 Heat of formation of  $\text{MnO}$  = 2984 B.t.u.  
 Heat generated =  $2984 \times 1047 = 3.12 \times 10^6$

Oxidation of silicon, weight = 488 lb.  
 Heat of formation of  $\text{SiO}_2$  = 11,693 B.t.u.

## Decomposition of improperly burned dolomite

Total weight of dolomite = 2500 lb.  
 Volatile = 15.54 per cent. = 389  
 Assumed 98 per cent. = 381 exists as  $\text{CO}_2$   
 To drive off  $\text{CO}_2$  = 1756 B.t.u. per lb.  
 Total heat to drive off  $\text{CO}_2$  =  $1756 \times 381 = 0.67 \times 10^6$

## THERMOPHYSICAL CHANGE

Hot metal = 65000 lb. Temperature =  $2474^\circ \text{F.}$   
 Tapping temperature =  $3080^\circ \text{F.}$  includes emissivity factor

Temperature rise ( $3080 - 2474$ ) =  $606^\circ \text{F.}$

Specific heat = 0.2

Heat absorbed =  $65,000 \times 606 \times 0.2 = 7.88 \times 10^6$

Scrap = 35,000 lb., temperature =  $62^\circ \text{F.}$

Melting temperature scrap =  $2795^\circ \text{F.}$

Heat required to bring to melting temperature =  $35,000 \times 2733 \times 0.16 = 15.30 \times 10^6$

Latent heat of fusion = 72 B.t.u.

Total heat of fusion =  $35,000 \times 72 = 2.52 \times 10^6$

Heat to raise to temperature of bath =  $(3080 - 2795) 35,000 \times 0.2 = 2.00 \times 10^6$

Total heat =  $19.82 \times 10^6$

## Total heat in molten slag

Heat in tapping slag =  $9254 \times 1066 = 9.86 \times 10^6 \text{ B.t.u.}$

Total heat absorbed =  $65.38 \times 10^6 \text{ B.t.u.}$

Heat generated =  $11,693 \times 488 = 5.71 \times 10^6$

Oxidation of phosphorus, weight = 126 lb.  
 Heat of formation of  $\text{P}_2\text{O}_5$  = 10,825 B.t.u.

Heat generated =  $10,825 \times 126 = 1.36 \times 10^6$

Heat of formation of slag, weight = 9254 lb.  
 Heat of formation of slag = 108 B.t.u.

Heat generated =  $108 \times 9254 = 1.00 \times 10^6$

Total heat generated =  $22.85 \times 10^6 \text{ B.t.u.}$

## AUTHORITIES FOR CONSTANTS USED

## THERMOCHEMICAL CHANGES

Iron oxide reduction—Richards  
 Decomposition of limestone—U. S. Bur. of Standards  
 Oxidation of C, Mn, Si, P—Richards, LeChatelier, Berthelot, Thomson  
 Formation of slag, calculated using Richards' values

## THERMOPHYSICAL CHANGES

Specific heat, pig iron—0.1665—Oberhoffer  
 Specific heat, soft steel—0.16—Meuthner  
 Latent heat of fusion, pig iron—Hutter  
 Latent heat of fusion, steel—average value—  
 Jetner, Richards, Brisker  
 Heat in molten slag—Springorum

## THERMAL BALANCE SHEET

## HEAT ABSORBED

Red. of oxides of Fe	= 20.93
Absorp. moist. of ore	= 2.42
Decomp. of limestone	= 3.57
Absorp. moist. of limestone	= 0.23
Decomp. of dolomite	= 0.67
Heat in molten slag	= 9.86
Heat added to mixer metal	= 7.88
Heat added to scrap	= 19.23

## HEAT GENERATED

Oxidation of C	= $11.66 \times 10^6$
Oxidation of Mn	= $3.12 \times 10^6$

Oxidation of Si	= $5.71 \times 10^6$
Oxidation of P	= $1.36 \times 10^6$
Heat form. slag	= $1.00 \times 10^6$
Balance heat to be supplied by combustion of gases in furnace	= $42.53 \times 10^6$
Total B.t.u.	= $65.38 \times 10^6$

## THERMAL EFFICIENCY OF BATH

Thermal efficiency of furnace = 17.3 per cent.  
 B.t.u. in gas per pound of coal = 10,625  
 Total B.t.u. to be supplied in producer gas =  $245.83 \times 10^6$   
 Total coal burned = 23,187 lb.



TABLE 10.—Continued  
THERMAL BALANCE SHEET

## HEAT ABSORBED

## THERMOCHEMICAL CHANGES

Reduction of oxides of iron	
Heat of formation of $\text{Fe}_2\text{O}_3$	= 3240
Heat of formation of $\text{FeO}$	= 2430
Input	
$\text{Fe}_2\text{O}_3$	= 6661
$\text{FeO}$	= 103
Heat of formation.	
$\text{Fe}_2\text{O}_3$	= $6661 \times 3240 = 21.58 \times 10^6 \text{ B.t.u.}$
$\text{FeO}$	= $108 \times 2430 = 0.26 \times 10^6 \text{ B.t.u.}$
Total	= $21.84 \times 10^6 \text{ B.t.u.}$
Output	
Tapping slag = $\text{FeO} = 3268 \times 2430$	= $7.94 \times 10^6$
Moisture in ore	
Total weight of ore	= 9170 lb.
Per cent moisture	= 8
Total water	= 734
Total heat to make steam at $212^\circ$	
$734 \times 1092$	= $0.80 \times 10^6 \text{ B.t.u.}$
Specific heat of steam $0.42 + 0.00013 (2800 + 212)$	= 0.81
Heat in superheat $734 (2800 - 212)$	= $0.81$
$1.54 \times 10^6 \text{ B.t.u.}$	
Total	= $2.34 \times 10^6 \text{ B.t.u.}$
Decomposition of limestone	
Heat of formation $\text{CaCO}_3$ per lb.	= 772 B.t.u.
Total limestone	= 11,675 lb.
Total heat required	= $11,675 \times 772 = 9.01 \times 10^6 \text{ B.t.u.}$
Moisture 1.5 per cent. = 175 lb.	
Total heat to make steam	=
$175 \times 1092$	= $0.19 \times 10^6$
Heat in superheat	=
$175 \times 2096$	= $0.37 \times 10^6$
Total	= $0.56 \times 10^6$

## Decomposition of improperly burned dolomite

Total weight of dolomite = 2500 lb.  
Volatile = 15.54 per cent = 389 lb.  
Assumed 98 per cent = 381 exists as  $\text{CO}_2$   
To drive off  $\text{CO}_2$  = 1756 B.t.u. per lb.  
Total heat to drive off  $\text{CO}_2$  =  $381 \times 1756 = 0.67 \times 10^6 \text{ B.t.u.}$

## THERMOPHYSICAL CHANGE

Hot metal = 65,000 lb Temperature =  $2474^\circ \text{F}$   
Tapping temperature =  $3080^\circ \text{F}$  includes emissivity factor  
Temperature rise  $(3080 - 2474) = 606^\circ \text{F}$ .  
Specific heat = 0.2  
Heat absorbed =  $65,000 \times 606 \times 0.2 = 7.88 \times 10^6 \text{ B.t.u.}$   
Scrap = 35,000 lb. Temperature =  $62^\circ \text{F}$ .  
Melting temperature scrap =  $2795^\circ \text{F}$ .  
Heat required to bring to melting temperature =  $35,000 \times 2733 \times 0.16 = 15.30 \times 10^6$   
Latent heat of fusion = 72 B.t.u.  
Total heat of fusion =  $35,000 \times 72 = 2.52 \times 10^6$   
Heat to raise to temperature of bath  $(3080 - 2795)$   $35,000 \times 0.2 = 2.00 \times 10^6$   
Total heat =  $19.82 \times 10^6$   
Total heat in molten slag  
Heat in tapping slag =  $15,465 \times 1066 = 16.49 \times 10^6 \text{ B.t.u.}$   
Total heat absorbed =  $70.67 \times 10^6 \text{ B.t.u.}$

## HEAT GENERATED

Oxidation of carbon, weight = 2669 lb  
Heat of formation of  $\text{CO}$  from  $\text{C}$  per lb = 4374 B.t.u.  
Heat generated =  $4374 \times 2669 = 11.67 \times 10^6$   
Oxidation of manganese, weight = 645 lb.  
Heat of formation of  $\text{MnO}$  = 2984 B.t.u.  
Heat generated =  $2984 \times 645 = 1.92 \times 10^6$   
Oxidation of silicon, weight = 483 lb.  
Heat of formation of  $\text{SiO}_2$  = 11,693 B.t.u.

Heat generated =  $11,693 \times 483 = 5.71 \times 10^6$   
Oxidation of phosphorus, weight = 129 lb.  
Heat of formation of  $\text{P}_2\text{O}_5$  = 10,825 B.t.u.  
Heat generated =  $10,825 \times 129 = 1.40 \times 10^6$   
Heat of formation of slag, weight = 15,465 lb.  
Heat of formation of slag = 74 B.t.u.  
Heat generated =  $15,465 \times 74 = 1.14 \times 10^6$   
Total heat generated =  $21.84 \times 10^6 \text{ B.t.u.}$

## AUTHORITIES FOR CONSTANTS USED

## THERMOCHEMICAL CHANGES

Iron oxide reduction—Richards  
Decomposition of limestone—U. S. Bur. of Standards  
Oxidation of  $\text{C}$ ,  $\text{Mn}$ ,  $\text{Si}$ ,  $\text{P}$ —Richards, LeChatelier, Berthelot, Thomson  
Formation of slag, calculated using Richards' values

## THERMOPHYSICAL CHANGES

Specific heat, pig iron—0.1655—Oberhoffer  
Specific heat, soft steel—0.16—Meuthner  
Latent heat of fusion, pig iron—Hutter  
Latent heat of fusion, steel—average value—  
Jetner, Richards, Brisker  
Heat in molten slag—Springorum

## THERMAL BALANCE SHEET

## HEAT ABSORBED

Red. of oxides of  $\text{Fe}$  = 13.90  
Absorp. moist. of ore = 2.34  
Decomp. of limestone = 9.01  
Absorp. moist. of limestone = 0.56  
Decomp. of dolomite = 0.67  
Heat in molten slag = 16.49  
Heat added to mixer metal = 7.38  
Heat added to scrap = 19.82

## HEAT GENERATED

Oxidation of  $\text{C}$  =  $11.67 \times 10^6$   
Oxidation of  $\text{Mn}$  =  $1.92 \times 10^6$

Oxidation of  $\text{Si}$  =  $5.71 \times 10^6$   
Oxidation of  $\text{P}$  =  $1.40 \times 10^6$   
Heat form. slag =  $1.14 \times 10^6$   
Balance heat to be supplied by combustion of gases in furnace =  $48.83 \times 10^6$   
Total B.t.u. =  $70.67 \times 10^6$

## THERMAL EFFICIENCY OF BATH

Thermal efficiency of furnace = 17.3 per cent.  
B.t.u. in gas per pound of coal = 10,625  
Total B.t.u. to be supplied in producer gas =  $48.83 \times 10^6 = 282.25 \times 10^6$   
0.173  
Total coal burned = 28,564 lb.





TABLE 12.—Continued  
THERMAL BALANCE SHEET

## HEAT ABSORBED

## THERMOCHEMICAL CHANGES

Reduction of oxides of iron  
Heat of formation of  $\text{Fe}_2\text{O}_3$  = 3240  
Heat of formation of  $\text{FeO}$  = 2430  
Input  
 $\text{Fe}_2\text{O}_3$  = 8034       $\text{FeO}$  = 131  
Heat of formation  
 $\text{Fe}_2\text{O}_3$  = 3240  $\times$  8034 = 26 03  $\times 10^5$   
 $\text{FeO}$  = 131  $\times$  2430 = 0.32  $\times 10^6$

Total = 26 35  $\times 10^6$

Output  
Tapping slag— $\text{FeO}$  = 2474  $\times$  2430 = 6 01  $\times 10^6$

Moisture in ore  
Total weight of ore = 11,060 lb.  
Per cent. moisture = 8  
Total water = 885  
Total heat to make steam at  
212° = 885  $\times$  1092 = 0.97  $\times 10^6$   
Specific heat of steam =  
0.42  $\div$  0.00013 (2800 - 212) = 0.81

Heat in superheat =  
885 (2800 - 212) 0.81 = 1.85  $\times 10^6$   
Total = 2.82  $\times 10^6$  B.t.u.

Decomposition of limestone  
Heat of formation  $\text{CaCO}_3$  per lb. = 772 B.t.u.  
Total limestone = 9520 lb.  
Total heat required = 9520  $\times$  772 = 7 35  $\times 10^6$

Moisture 1.5 per cent. = 142  
Total heat to make steam =  
142  $\times$  1092 = 0.16  $\times 10^6$

Heat in superheat =  
142  $\times$  2096 = 0.30  $\times 10^6$

Total = 0.46  $\times 10^6$  B.t.u.

## Decomposition of improperly burned dolomite

Total weight of dolomite = 2300 lb.  
Volatile = 15.54 per cent. = 389  
Assumed 98 per cent = 381 exists as  $\text{CO}_2$   
To drive off  $\text{CO}_2$  = 1756 B.t.u. per lb.  
Total heat to drive off  $\text{CO}_2$  = 1756  $\times$  381 = 0.67  $\times 10^6$

## THERMOPHYSICAL CHANGE

Hot metal = 65,000 lb., temperature = 2474° F.  
Tapping temperature = 3080° F. includes emissivity factor

Temperature rise (3080 - 2474) = 606° F.

Specific heat = 0.2

Heat absorbed = 65,000  $\times$  606  $\times$  0.2 = 7 88  $\times 10^6$

Scrap = 35,000 lb. Temperature = 62° F.

Melting temperature scrap = 2795° F.

Heat required to bring to melting temperature =

35,000  $\times$  2733  $\times$  0.16 = 15 30  $\times 10^6$

Latent heat of fusion = 72 B.t.u.

Total heat of fusion =  
35,000  $\times$  72 = 2 52  $\times 10^6$

Heat to raise to temperature of bath =

(3080 - 2795)  $\times$  35,000  $\times$  0.2 = 2.00  $\times 10^6$

Total heat = 19.82  $\times 10^6$

Total heat in molten slag

Heat in tapping slag = 14,318  $\times$  1066 = 15.26 B.t.u.

Total heat absorbed = 74.80  $\times 10^6$  B.t.u.

## HEAT GENERATED

Oxidation of carbon, weight = 2667 lb.  
Heat of formation of  $\text{CO}$  from  $\text{C}$  per lb. = 4374 B.t.u.

Heat generated = 4374  $\times$  2667 = 11.67  $\times 10^6$

Oxidation of manganese, weight = 645 lb.

Heat of formation of  $\text{MnO}$  = 2984 B.t.u.

Heat generated = 2984  $\times$  645 = 1.92  $\times 10^6$

Oxidation of silicon, weight = 488 lb.

Heat of formation of  $\text{SiO}_2$  = 11,693 B.t.u.

Heat generated = 11,693  $\times$  488 = 5.71  $\times 10^6$

Oxidation of phosphorus, weight = 435 lb.

Heat of formation of  $\text{P}_2\text{O}_5$  = 10,825 B.t.u.

Heat generated = 10,825  $\times$  435 = 4.71  $\times 10^6$

Heat of formation of slag, weight = 14,435 lb.

Heat of formation of slag = 191 B.t.u.

Heat generated = 191  $\times$  14,435 = 2.76  $\times 10^6$

Total heat generated = 26.77  $\times 10^6$  B.t.u.

## AUTHORITIES FOR CONSTANTS USED

## THERMOCHEMICAL CHANGES

Iron oxide reduction—Richards  
Decomposition of limestone—U. S. Bur. of Standards  
Oxidation of  $\text{C}$ ,  $\text{Mn}$ ,  $\text{Si}$ ,  $\text{P}$ —Richards, LeChatelier, Berthelot, Thomson  
Formation of slag, calculated using Richards' values

## THERMOPHYSICAL CHANGES

Specific heat, pig iron—0.1665—Oberhoffer  
Specific heat, soft steel—0.16—Mauther  
Latent heat of fusion, pig iron—Hutter  
Latent heat of fusion, steel—average value—  
Jetner, Richards, Brisker  
Heat in molten slag—Springorum

## THERMAL BALANCE SHEET

## HEAT ABSORBED

Red. of oxides of Fe = 20.34  
Absorp. moist. of ore = 2.82  
Decomp. of limestone = 7.85  
Absorp. moist. of limestone = 0.46  
Decomp. of dolomite = 0.67  
Heat in molten slag = 15.26  
Heat added to mixer metal = 7.88  
Heat added to scrap = 19.82

## HEAT GENERATED

Oxidation of  $\text{C}$  = 11.67  $\times 10^6$   
Oxidation of  $\text{Mn}$  = 1.92  
Oxidation of  $\text{Si}$  = 5.71

Oxidation of  $\text{P}$  = 4.71

Heat form. slag = 2.76

Balance heat to be supplied by combustion of  
gases in furnace = 47.83  $\times 10^6$   
Total B.t.u. = 74.60  $\times 10^6$

## THERMAL EFFICIENCY OF BATH

Thermal efficiency of furnace = 17.3 per cent.

B.t.u. in gas per pound of coal = 10,625

Total B.t.u. to be supplied in producer gas =

47.83  $\times 10^6$  = 276.47  $\times 10^6$  B.t.u.

0.173

Total coal burned = 26,021 lb.

may most conveniently be ascertained by taking an average composition of those slags that, under given conditions, have yielded economical operation, and empirically separating it into a silicate slag (which is assumed to hold the phosphate slag in solution) and a phosphate slag, in which the phosphorus is assumed to be combined with calcium oxide in the form of  $\text{Ca}_4\text{P}_2\text{O}_8$ . When this has been done, the analysis of the silicate slag is calculated, and from this the relation of the silica to the lime plus magnesia and to the weight of the silicate slag is determined. The total weight of slag, of course, is the weight of the silicate slag plus the phosphate slag, the last named being the weight of the phosphorus oxidized multiplied by 5.9. In our operation, the average composition of generally satisfactory slags shows a silicate portion which analyzes as follows:  $\text{SiO}_2$ , 19 per cent.;  $\text{FeO} + \text{MnO}$ , 27 per cent.;  $\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{S}$ , 2 per cent or a total of 48 per cent. Therefore, the  $\text{CaO} + \text{MgO}$  necessary to equal 100 per cent. is, by difference, 52 per cent., and the  $\text{CaO} + \text{MgO}$  required per unit of  $\text{SiO}_2$  is the ratio of 52 to 19 or 2.74; and the weight of silicate slag produced per unit of silica is the ratio of 100 to 19 or 5.26. These ratios are used in all the theoretical heats shown, except in the excessive limestone charge, where they become silicate slag to silica 7.1, and  $\text{MgO} + \text{CaO}$  to  $\text{SiO}_2$  4.01. In all cases the ratio of phosphorus to calcium oxide is 1 to 3.61, which corresponds to the composition of the tetrabasic phosphate. Tables 13 and 14 give the ratios and the analyses of the theoretical slags used in the construction of the chemical and thermal balances and cost sheet.

Constructing a slag in this manner gives only the combined percentages of ferrous oxide and manganous oxide, so that it is necessary to compute on the basis of working conditions the quantity of residual manganese carried by the bath for different conditions of slag volume. With this amount ascertained, the manganese in the slag is the total manganese charged less that in the bath less that carried away by the furnace gases. The difference between the manganese in the slag, expressed as manganous oxide, and 27 per cent. is the ferrous oxide in the silicate slag.

TABLE 13.—*Slag Ratios*

	Silicate Slag						Phosphate Slag	
	$\text{SiO}_2$ , Per Cent.	$\text{FeO} +$ $\text{MnO}$ , Per Cent.	$\text{Al}_2\text{O}_3 +$ $\text{S}$ , Per Cent.	$\text{CaO} +$ $\text{MgO}$ , Per Cent.	Sil. Slag $\text{SiO}_2$	$\text{CaO} + \text{MgO}$ $\text{SiO}_2$	$\text{CaO}$ P	Phos. Slag P
Dichmann.....	21.0	26.00	4.0	49.00	4.78	2.33	3.61	5.9
In normal heats, values used.....	19.0	27.00	2.0	52.00	5.26	2.74	3.61	5.9
In excess limestone heat.....	14.0	27.00	2.0	57.00	7.10	4.00	3.61	5.9

TABLE 14.—*Analysis of Theoretical Slags*

	P <sub>2</sub> O <sub>5</sub> Per Cent.	FeO Per Cent.	MnO Per Cent.	SiO <sub>2</sub> Per Cent.	Al <sub>2</sub> O <sub>3</sub> + TiO <sub>2</sub> Per Cent.	CaO Per Cent.	MgO Per Cent.	S Per Cent.
Scrap.....	3.83	17.26	7.07	17.15	0.52	44.29	8.67	0.25
Standard iron, high SiO <sub>2</sub> .....	2.58	19.51	5.69	17.94	1.41	43.46	9.77	0.25
Standard iron, low SiO <sub>2</sub> .....	3.18	18.32	6.70	17.61	1.62	41.77	11.52	0.25
High-manganese iron, high SiO <sub>2</sub> .....	2.47	15.44	9.84	17.80	1.43	43.12	9.54	0.25
High-manganese iron, low SiO <sub>2</sub> .....	3.12	13.11	11.72	17.48	1.69	41.44	11.38	0.25
Excess limestone....	1.91	21.12	4.54	13.39	1.16	50.13	7.51	0.25
High-silicon iron....	1.42	22.37	3.64	18.31	1.09	46.24	6.18	0.25
High-phosphorus iron.	6.96	17.28	4.87	15.60	1.33	46.08	8.32	0.25
Average not including high limestone.....	3.36	17.61	7.07	17.41	1.30	43.77	9.34	0.25

The method of calculating the residual manganese is as follows: The residual manganese remaining in a bath, after the reactions have come to a condition of equilibrium, is a function of the manganese available (*i.e.*, the manganese charged less that which has been oxidized and carried away with the waste gases) the character of the slag, and the relative volumes or masses of slag and bath. The character of the slag determines the chemical affinity for manganese and represents the amount in the slag, other things being equal. But superimposed upon this is the relative masses of slag and bath, for a large slag volume will leave lower manganese residuals than one of similar analysis but smaller volume. For slags of similar analysis, it is considered that the manganese available will divide according to the relative masses.

Let  $\frac{\text{Weight manganese in bath}}{\text{Weight manganese in slag}} = x$  and  $\frac{\text{Weight of bath}}{\text{Weight of slag}} = s$

So it becomes necessary to determine the relation between  $x$  and  $s$  which is a measure of the chemical affinity and will remain essentially constant for a given type of slag. It was found, from practice, when working with slags of this type, that  $s = 22.5x$ .

Let  $a$  = weight of manganese in bath;

$b$  = weight of manganese in slag;

$$\frac{a}{b} = x$$

$a + b = y$  = total weight of manganese available.

$$b = y - bx$$

$$b = \frac{y}{1 + x}$$

$$a = y - \frac{y}{1 + x}$$

$$a = \frac{xy}{1 + x}$$

In all cases the ratio of bath to slag is known, so that it becomes possible to figure all the residuals on the same basis.

The effect of the various percentages of residual manganese on the finishing additions of manganese made in the ladle is shown in Table 15. The calculated amounts of pure manganese correspond to results obtained in actual practice.

TABLE 15.—*Effect of Residual Manganese on Manganese Added in Ladle*

	Residual Manganese, Per Cent.	Tons Ingot	Weight Manganese in Bath, Pounds	Weight Manganese, Required Pounds	Theoretical Added Manganese, Pounds	Actual Pounds Manganese in Ladle		Pounds 80 Per Cent. FeMn
						Ton	Heat	
Scrap.....	0.24	40.90	232	386	154	7.8	319	399
Standard iron, high SiO <sub>2</sub> .....	0.20	42.36	198	396	198	10.0	424	530
Standard iron, low SiO <sub>2</sub> .....	0.23	42.57	230	398	168	8.5	362	453
High-manganese iron, high SiO <sub>2</sub> ....	0.34	42.44	338	397	59	2.9	123	154
High-manganese iron, low SiO <sub>2</sub> ....	0.40	42.70	399	399	0	1.0	43	54
Excess limestone....	0.16	41.97	157	393	236	12.0	504	630
High-silicon iron....	0.12	42.04	118	394	276	14.0	589	736
High-phosphorus iron	0.16	42.53	159	398	239	12.0	510	638

It is to be emphasized that a residual manganese in excess of 0.25 per cent. not only reduces the open-hearth cost per ton of ingots by decreasing the quantity of expensive ferromanganese that must be added to the heat to attain a given manganese percentage, but because of the protection it gives against overoxidation in the furnace, the quality of the steel is improved. This higher quality steel increases the percentage of merchantable product at the mills by from 1 to 3 per cent., depending on the amount that the residual manganese exceeds 0.25 per cent.; and while such a saving cannot be properly shown on the open-hearth cost sheet, it increases the net profits of the works as a unit. The protection afforded against overoxidation by a proper percentage of residual manganese may be accounted for by the following reasoning: The oxygen of the ore first attacks the manganese, phosphorus, and silicon and at the higher temperatures the carbon oxidation takes precedence. As the carbon content of the bath decreases, iron oxidation sets in; and at the lower carbon percentages the protective power of carbon oxidation is very low. It seems apparent, therefore, that in the lower carbon ranges the 0.25 to 0.40 per cent. manganese, which at all temperatures is more easily

oxidized than iron, can act only as a preventive of overoxidation of the steel.

The weight of iron oxidized and carried away in the waste gases was taken in all ore heats to be 100 lb. per heat and the quantity of manganese lost in a similar way to be about 200 lb. per heat, in the cases of the high-manganese iron, and about 100 lb. per heat in the others. In the case of the scrap heat, these losses were taken at 150 lb. per heat for both iron and manganese.

As a matter of precaution, the percentage of phosphorus remaining in the steel, in the case of the high-phosphorus iron heat, was placed at 0.03 per cent. instead of 0.01 per cent. The sulfur content of all the slags was put at 0.25 per cent., which is both conservative and common in practice. All the calcium, magnesium, and aluminum oxides carried in with the charge appear in the slag.

Sulfur elimination in the open-hearth furnace is, at best, an uncertain and costly procedure. In the earlier days of the industry, when the use of natural gas was general, high-grade producer coal was available for those plants outside the gas belt and scrap heats more generally charged; there was then but little difficulty in holding the sulfur content of the steel at 0.04 per cent. and below, provided that the sulfur in the iron corresponded approximately to this percentage. With the advent of the higher percentage iron charges and lower grade fuel, the difficulty of producing low-sulfur steel has been tremendously increased. While probably sulfur above 0.04 per cent. is not, in many instances, prejudicial to the physical quality of the steel, the general trend of specifications is in the direction of lower, rather than higher, sulfur content. Regardless of the merits of either side of this controversy, one must meet specifications as they exist. Under such conditions and with low-manganese iron (1.00–1.25 per cent.) the percentage of sulfur in the pig iron must be practically as low as that desired in the steel.

As coke also has followed the downward trend in quality, it has become more difficult for the blast furnaces to produce consistently iron with the sulfur content desired by the open hearth, and this difficulty is increased by the necessity of maintaining a silicon content in the iron not appreciably above 1 per cent.

Under a condition of approximately 1 per cent. manganese and 0.05 per cent. sulfur in the iron and a sulfur content of 0.04 per cent. being required in the steel, or with a like manganese content and 0.04 per cent. sulfur in the iron and 0.035 per cent. sulfur or under being required in the steel, the open hearth is forced to adopt one of two methods of sulfur elimination, both of which are uncertain and costly. The usual method is to charge additional limestone, probably because the expense incurred is not so obvious as when ferromanganese is used. The cost sheet shows an increased cost of \$0.87 per ton in the case of the heat heavily over-

charged with limestone compared to the so-called standard heat charged with a normal amount, and the same relative increase of cost would have followed any proportional increase or decrease in the excess charged. Assuming that to accomplish an equal reduction in sulfur it has been necessary to use 10 lb. of pure manganese per ton of ingots, the cost of such sulfur removal added to the cost of ingots in the case of the standard iron heat would bring the total cost to \$31.43. This figure is \$0.14 lower than the cost of the limestone heat, although it has not been credited with the reduced ladle addition of manganese, and the improvement in the quality of the steel.

It will be observed on the chemical balance sheet that all irons are assumed to carry 0.04 per cent. sulfur, but that the steel produced with the 2-per cent. manganese iron contains 0.035 per cent. sulfur, which is more than would result in practice under the conditions of charge and fuel assumed. Whether the open hearth is required to produce 0.035 per cent. and under sulfur in the steel from 0.04-per cent. sulfur iron, or 0.04 per cent. sulfur in the steel from 0.05-per cent. sulfur iron, the cost of accomplishing this is, in all cases, less with 2-per cent. manganese than with 1-per cent. manganese iron. Furthermore, because of the sulfur eliminated from the high-manganese iron in the transfer ladle between the blast furnaces and the open hearth and in the open-hearth mixer, 0.04-per cent. sulfur steel can be regularly and economically produced from such iron, even though its sulfur content rises to 0.07 per cent.

With the thought of presenting greatly contrasting costs and thus emphasizing the loss sustained through the charging of unnecessarily high-silicon irons, the silicon content of all the irons has been assumed at 0.75 per cent.; such an amount is not only practical but desirable in the case of the 2-per cent. manganese iron. On the other hand, 0.75 per cent. silicon iron with 1 per cent. manganese would, in actual practice, cost more to produce than an iron containing 0.75 per cent. silicon and 2 per cent. manganese; and, unless made very hot physically at the expense of increased coke charges, the works as a unit would suffer a loss because of delayed operations and excessive scrap, from badly skulled ladles, mixers, and runners.

In the case of the high-silicon iron heat, the assumption of the use of 1.75-per cent. silicon iron may be radical, but the use of such iron is not as unusual as may be supposed; and while the physical results of its use in the open hearth may be readily perceived, its effect on costs is not usually considered.

While the costs of the low-silica ore heats do not strictly come within the province of a paper dealing with metalloids, they are shown to emphasize the harmful effect of such unnecessary impurities upon practice and costs. In the case shown, the difference in cost between the so-called standard iron heat, and the low-silica ore heat was \$0.43 per ton of

ingots in favor of the latter. It is apparent from this that if low-silica ore can be procured at the same cost as the high-silica ore, the use of the last named is nothing short of criminal waste.

In closing, I wish to acknowledge the help given in the preparation of this paper by my assistant, Roger B. McMullen, Jr.

## DISCUSSION

V. J. PAZZETTI,\* Bethlehem, Pa. (written discussion).—The author has done an immense amount of calculating and has outlined some typical heats in admirable form for study and criticism. The paper is a valuable contribution to the literature of the basic open-hearth process because it discusses many of the important variables that enter into the costs of ingots made by several of the numerous possible combinations of raw material.

Some important factors enter into the costs of finished steel that are not dwelt upon in the paper; of these may be mentioned: The relative costs of iron and scrap, the time from tap to tap, the cost of furnace upkeep, and the desired characteristics of the steel. All of these materially affect the ultimate cost of the finished product and must be considered when specifying the composition limits of the various metalloids in the pig iron.

Considering all these factors and responding more particularly to the inquiry of the blast-furnace operator concerning the reasons for the basic open-hearth operator's specification limitations on the five metalloids mentioned by the author, it seems possible, in a measure, to supplement his discussion.

The carbon content of the pig iron, so long as it is regular, does not offer a serious problem in the open-hearth process. A high percentage of total carbon, however, can usually be regarded as an indication of satisfactory blast-furnace operation and as an index of iron that is "good" both physically and chemically; whereas an iron lean in carbon will be usually inferior for basic open-hearth use.

The open-hearth operators' specifications for manganese and silicon are greatly influenced by the four considerations named above, and by the nature of the process he is using.

To exemplify the influence of the kind of process used, let us consider the case of manganese in a process using a run-off slag (the second practice mentioned on p. 144). With the run-off slag, the advantages of 2.00 per cent. manganese in the pig iron, as shown in the fifth theoretical heat, would disappear, as the run-off slag would carry out so much manganese as to make impossible the retention in the bath of as much as

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0.40 per cent. manganese. There would be added, the disadvantage that in most locations pig iron containing 2.00 per cent. manganese costs more to make than pig iron containing half that quantity.

For conditions where over 50 per cent. scrap is carried and heats therefore made without run-off slag, 1.50 per cent. manganese is more beneficial in making standard commercial steels than 1.00 per cent. manganese. In such cases, the ingot cost due to the pig iron component of the charge is increased but little by the extra 0.50 per cent. manganese. As there is no run-off slag, there is some residual manganese which does act to curtail the amount of recarburizing ferromanganese needed. The presence of a substantial percentage of manganese throughout the operation protects the iron from oxidation and aids in removal of the sulfur, some of which is being continually imparted by the fuel.

To exemplify the influence of the character of product on the pig iron specification, we can consider the manufacture of high-grade steels, where the additional cost of pig iron containing above 2.00 per cent. manganese is a less important consideration. In such cases, the desulfurizing effect in the iron transfer ladle, noted by the author, also comes into evidence, and better surface condition of the steel during rolling may be expected.

In discussing the silicon content, it is again necessary to consider the conditions governing the proportion of iron to scrap in the charge. The author's first theoretical heat seems hardly practicable under the conditions he shows. If the silicon in the pig iron is as low as 0.75 per cent. and the iron forms only 35 per cent. of the charge, we would hardly expect to be able to melt with as much as 0.50 per cent. carbon in the bath. With such low iron proportion, in order to get action in the early part of the bath and to protect the carbon from disappearing, we would expect to be benefitted by 1.25 per cent. silicon content of pig iron; or if we were confined to 0.75 per cent. silicon iron, we should wish to increase the iron proportion and decrease the scrap.

In the seventh theoretical heat, the author shows by, perhaps, extreme figures, the large increased lime addition and consequent slag volume needed when 1.75 per cent. silicon iron forms 65 per cent. of the charge; in order to eliminate the silicon from the bath. The large loss of iron in the slag and the consequently diminished yield of ingots and the increased costs of fuel (in which he has no doubt allowed without explaining it) for the lengthened time of heat and of slag disposal are reckoned in the table. Apparently the limestone additions were reckoned high enough to allow the assumption that the furnace lining would be so protected by excess lime that only normal erosion would occur. The increased cost of furnace lining upkeep due to the use of high-silicon pig iron, which cost he does not show, might then be assumed to be included in the other increased cost items mentioned.



An unmentioned comment on pig-iron composition might well be emphasized; that is, where direct hot metal is used with a mixer of small capacity. Here blast-furnace irregularities that vary the pig-iron composition, and particularly the silicon from cast to cast, increase the cost of ingots. If the steelmaker charges sufficient lime to care for expected high silicon in the iron and the iron drops in silicon, he has added an hour or two to the time needed to make the heat. Further, even if he has charged sufficient lime for increased silicon in the pig iron, his furnace linings suffer from the excess silicon before the lime can come up to counteract it.

Increasing the phosphorus content of the iron two and a half times, as in the eighth theoretical heat, has less effect on the ingot cost than increasing the silicon content one and three quarters times. We do not find much difficulty with pig irons containing less than 0.30 per cent. phosphorus and, therefore, do not feel forced to specify as low as 0.20 per cent. phosphorus.

Each of the theoretical heats assumes 0.04 per cent. sulfur and under in the product. In most steel-producing locations, considerable cost is involved to attain this low figure. Although no facts are available that prove that steels with 0.06 per cent. sulfur are unsuitable for most uses, some steel purchasers distrust steels of that composition. The fact that the steel bath takes up sulfur from the fuel requires one of two things: Either that the pig iron contain no greater content of sulfur than is allowed in the finished steel, or that manganese be used in some form to eliminate the sulfur. Both methods are costly. The first requires additional lime burden and increased coke consumption at the blast furnace—with consequently increased cost of pig iron. The second requires the increased use of manganese in one form or another in the open hearth, an expensive addition whichever way it is used. Sulfur can be kept low at less cost in the blast furnace than in the open-hearth furnace.

Considering the time of basic open-hearth heats from tap to tap and the influence exerted on the specified composition of basic pig iron, we must, among other things, consider local conditions. In localities where pig iron is cheaper than scrap, and in some localities where high-manganese iron costs no more than low-manganese iron, the percentage of pig iron in the charge is increased and the run off of slag is made to reduce the time of heats. The time saving is great enough to pay the cost of the large iron and manganese losses that occur.

Where scrap is cheaper than pig iron, the percentage of scrap is increased and the necessity for the run-off slag disappears because of the smaller slag volume. For heats made without the run-off slag, the pig-iron specification would call for higher silicon and manganese than for heats made with a run-off slag. In a locality operating under the latter

conditions, basic pig iron is usually specified as follows: Carbon, not specified; manganese, 1.50 per cent. (average); silicon, 1.00 per cent. (average); phosphorus, 0.30 per cent. and under; sulfur, 0.04 per cent. and under.

In this same locality, the operations of a recent month showed average residual manganese to be 0.22 per cent. when average manganese in pig iron was 1.65 per cent. The pig iron averaged 51.27 per cent. of the charge. The average pig-iron silicon was 1.24 per cent. Further details for this month's practice are shown in Table 16.

TABLE 16.—*Open-hearth Practice for an Entire Month in 1923*  
(Steel Plant Operating without Run-off Slag)

CHARGE			ANALYSIS OF CHARGE		
	POUNDS	PER CENT.			PER CENT.
Hot metal..	100,000	51.27	Hot metal		
Steel scrap ..	90,000	44.03	Silicon. ....		1.24
Manganese ..	1,000 in bath	1.14	Manganese ..		1.65
Manganese ..	1,600 ladle.		Phosphorus..		0.144
50 per cent silicon ..	200		Sulfur.....		0.040
Ore charged ..	12,000	3.56	Steel scrap		
Ore fed. . . .	6,000		Carbon.....		0.12
Limestone ..	17,500		Manganese ..		0.53
		9.60	Phosphorus ..		0.030
			Sulfur....		0.050

TIME OF HEATS			LIMESTONE		
	Hour	Minute			PER CENT.
Before hot metal. . . . .	3	00	Limestone		
After hot metal....	7	52	Silica... ..		1.00
	—	—	Ore		
Total time of heat .. . . .	10	52	Iron... ..		64.56
			Manganese..		0.10
			Phosphorus..		0.074
			Sulfur.....		0.024
			Silica.....		2.88
			Aluminum.....		0.73

PRACTICE OF HEATS			ANALYSIS OF HEATS AT TAPPING		
		PER CENT.			PER CENT.
Ingot yield..		89.32	Carbon.....		0.10
Scrap.....		3.60	Residual manganese....		0.22
Loss..		7.08	Phosphorus.....		0.020
Average tons per heat. ....		81.2	Sulfur.....		0.050

ANALYSIS, TAPPING SLAGS			FINAL ANALYSIS OF HEATS		
		PER CENT.			PER CENT.
SiO <sub>2</sub> .....		15.0	Carbon ..		0.18
FeO ..		19.0	Manganese.....		0.69
CaO ..		43.0	Phosphorus ..		0.018
MgO ..		8.0	Sulfur.....		0.047
MnO... ..		7.0			
P <sub>2</sub> O <sub>5</sub> .....		2.0			

REMARKS No run-off slag; heats melted at about 0.50 per cent. carbon.

In a plant using a run-off slag, the records of five carefully observed experimental heats showed average residual manganese to be 0.09 per

cent. when average manganese in pig iron was 1.69 per cent. The pig iron averaged 63.1 per cent. of the charge. The average pig-iron silicon was 0.99 per cent. Further details are shown in Table 17.

TABLE 17.—Average Record of Five Experimental Heats  
(Made at a Steel Plant with Run-off Slag)

CHARGE			ANALYSIS OF CHARGE		
	Pounds	PER CENT.			PER CENT.
Hot metal.....	125,460	63.12	Hot metal		
Steel scrap.....	52,780	26.61	Silicon.....		0.99
Manganese.....	840	0.35	Manganese.....		1.69
Fine ore.....	31,480	9.92	Phosphorus.....		0.292
Hard ore.....	4,265		Sulfur.....		0.028
Limestone.....	14,060	7.1	Steel scrap		
			Carbon.....		0.14/0.25
			Manganese.....		0.35/0.50
			Phosphorus.....		0.014
			Sulfur.....		0.033

TIME OF HEATS			LIMESTONE		
	Hour	MIN-UTE			PER CENT.
Before hot metal.....	2	12	Limestone		
After hot metal.....	6	12	Silica.....		0.79
	—	—	Lime.....		54.00
Total.....	8	24	MgO.....		0.88
			Al.....		0.40
			Fine ore		
			Silica.....		6.67
			Manganese.....		0.38
			Aluminum.....		1.85
			Iron.....		53.85
			Phosphorus.....		0.076
			Hard ore		
			Silica.....		4.18
			Manganese.....		0.19
			Aluminum.....		0.36
			Iron.....		64.30
			Phosphorus.....		0.152

PRACTICE OF HEATS			FINAL ANALYSIS OF HEATS		
		PER CENT.			PER CENT.
Open-hearth ingots.....		88.0	Carbon.....		0.13
Scrap.....		3.4	Manganese.....		0.89
Loss.....		8.6	Phosphorus.....		0.014
Average tons per heat.....		78.0	Sulfur.....		0.029

SLAG ANALYSIS			BATH ANALYSES			
	RUN-OFF SLAG, PER CENT.	TAPPING SLAG, PER CENT.		CAR- BON, PER CENT.	MAN- GANESE, PER CENT.	PHOS- PHORUS, PER CENT.
Silica.....	23.56	15.62	First hour.....	2.94	0.02	0.032
Iron.....	27.06	16.86	Second hour.....	2.44	0.02	0.014
Lime.....	17.47	44.03	Third hour.....	1.72	0.03	0.015
MgO.....	5.04	9.23	Fourth hour.....	1.08	0.06	0.017
Manganese.....	11.30	4.17	Fifth hour.....	0.50	0.08	0.014
Phosphorus.....	0.93	0.66	Sixth hour.....	0.08	0.09	0.011
Sulfur.....	0.12	0.18				0.028

GEORGE B. WATERHOUSE,\* Cambridge, Mass.—The most harmful elements, the most harmful metalloids, in regard to basic practice are silicon and sulfur, and of these perhaps silicon is the one that varies the most and gives the most trouble. It increases the slag volume; it makes heats melt with high carbon where one would expect them to melt with a normal carbon and get the regular practice; it affects the time of the process very considerably. The author has shown this fact in connection with the coal consumption; heats that require more time naturally require more coal to bring them to proper tapping condition. For instance, he shows a variation from 470 lb. per ton up to 720 lb., which variation is usually due to the variation in silicon. But of the metalloids that are most directly harmful to basic practice, sulfur is the one to be most feared, on which fact the author lays proper emphasis.

C. L. KINNEY, JR. (author's reply to discussion).—The amount of coal per heat or per ton of ingots given in this paper was based on a furnace efficiency of 17.3 per cent., as shown in the paper of C. L. Kinney, Jr. and G. R. McDermott.<sup>3</sup> A recalculation of this heat balance based on the following data results in an efficiency of 16.1 per cent.

The heats of formation of  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$  shown were per pound of iron but were used as per pound of oxide. The correct heat of formation of  $\text{Fe}_2\text{O}_3$  per pound of oxide is 2200 B.t.u. and of  $\text{FeO}$  1643 B.t.u. The result of using these figures, which are considerably lower than the others, is to decrease the heat absorbed by the charge and, consequently, with a fixed coal consumption to lower the percentage efficiency of the furnace. In the same figure, the heat necessary to bring the  $\text{CO}_2$  liberated from the partly burned dolomite and the calcination of the limestone up to temperature was left out. This means an increase in the amount of heat absorbed by the charge and, consequently, with a fixed coal consumption an increase in the furnace efficiency, which counteracts to some extent the above-mentioned decrease.

This corrected furnace efficiency has been applied to all heats in the present paper and the correct heats of formation of the iron oxides and the heat absorbed by the  $\text{CO}_2$  have been taken into consideration. Further, in Table 5, the amount of moisture charged in the limestone should be 35 instead of 351 lb.; this reduces the heat absorbed by the moisture of the limestone to one-tenth of that shown. In Table 2, the percentage loss in melting of the scrap heat should be 3.38 per cent. instead of 4.38 per cent.; this makes the ingot percentage 92.62 per cent. instead of 91.62 per cent. and the tons of ingots produced 41.35 instead of 40.90, thus lowering the cost per ton of the scrap heat.

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\* Professor of Metallurgy, Massachusetts Institute of Technology.

<sup>3</sup> Thermal Efficiency and Heat Balance of an Open-hearth Furnace. *Year Book, Amer. Iron and Steel Inst.* (1922), Fig. 6.

The effect of these corrections on the cost per ton and condensed thermal balance sheet is shown by the following recalculated tables:

TABLE 18

Type of Heat	Original Cost	Corrected Cost	Difference
Scrap.....	\$29.11	\$28.91	\$0.20
Standard iron....	30.70	30.70	0 00
Standard iron, low-silica ore.....	30.27	30.23	0.04
High-manganese iron.....	30.27	30.38	0.11
High-manganese iron, low-silica ore...	29.77	29.67	0.10
Excess limestone.....	31.57	31.68	0 11
High-silicon iron.....	32.21	32.31	0.10
High-phosphorus iron .....	31.12	31.11	0.01

TABLE 19

Type of Charge	Heat Absorbed, Millions B.t.u.	Heat Generated, Millions B.t.u.	Heat to be Supplied in Furnace, Millions B.t.u.	At 18.1 Per Cent. Effective Heat to be Supplied in Gas, Millions B.t.u.	At 10,625 B.t.u. per Pound, Total Pounds Coal per Heat	Pounds Coal per Ton Ingots	At 17.3 Per Cent Efficiency, Pounds Coal per Ton Ingots
Scrap.....	47.13	11.71	35.42	220.00	20,706	501	467
Standard-iron high-silica ore.....	61 79	21.77	40 02	248.57	23,395	552	551
Standard-iron, low-silica ore.....	57.75	21.43	36 32	225.59	21,232	499	511
High-manganese iron, high-silica ore.....	66.51	23.27	43 24	268.57	25,277	596	583
High-manganese iron, low-silica ore.....	60 25	22.85	37.40	232.30	21,864	512	542
Excess limestone...	69.83	21.84	47.99	293.07	28,054	668	633
High-silicon iron.	84.15	30.20	53.95	335.09	31,538	780	720
High-phosphorus iron	71.07	26.77	44 30	275.16	25,897	609	612

Mr. Pazetti's discussion of the subject matter of the paper is valuable inasmuch as it emphasizes certain conventional practices, which cause grave economic losses to the basic open-hearth process. He seems to feel that certain practical phases of the comparative costs, such as relative time of heats, etc., have not been given due consideration, therefore I would like to emphasize the fact that in a paper dealing with the technical aspects of changes in charge composition it was essential that the real issue should not be beclouded with too much operating detail; for while it is true that variations in operating characteristics play an important part in the daily work of an open-hearth plant, it is, unfortunately, a fact that their manifestations are too frequently taken as the disease instead of as minor symptoms. For these reasons it was

necessary to put all heats upon a calculated basis and standardize the prices for iron and scrap. The matter of decrease or increase in the time per heat, while not specifically referred to in terms of hours and minutes, was reflected by the pounds of coal per ton of ingots.

Mr. Pazetti advances the opinion that heats charged with high percentages of high-manganese iron are not economical because the loss of manganese in the run-off slag is so great that the residual manganese in the bath differs little from that prevailing when 1 per cent. manganese iron is charged instead of 2 per cent. He shows, in substantiation of this statement, the record of five heats made with a 63 per cent. charge of 1.69 per cent. manganese iron with an average residual manganese of 0.09 per cent., which is startling when one considers that in my papers a charge of 65 per cent. iron of 2 per cent. manganese content and no run-off slag shows a residual manganese of 0.40 per cent. I am willing to agree that commercial expediency perhaps demands that a run-off slag be used and that when such a method is used it is not possible to obtain a 0.40 per cent. residual manganese, but I must emphatically disagree with Mr. Pazetti when he quotes a 0.09 per cent. residual manganese as representative of good practice with high-manganese irons and run-off slags and implies that such a manganese content in the iron does not justify itself. The contributing causes for such a remarkably low percentage of residual manganese must be: an excessive slag volume; overcharged furnaces which necessitate a larger percentage of run-off slag than is justifiable by good practice; and the physical character of the initial ore charged, it being a well known fact that very fine ores high in moisture give rise to explosive reactions and thereby abnormal increases in the percentage of run-off slag.

Mr. Pazetti does not give the amount of dolomite used per ton of ingots, but it appears that his limestone charge (179 lb. per ton of ingots) is within the limits of good practice and one must of necessity assume that the low residual manganese shown was caused not by too great a slag volume but by a premature running off of the run-off slag, perhaps unavoidable, on account of concomitant physical conditions. The difference between the two plans of using high-manganese iron is clearly shown by Table 20.

Mr. Pazetti again takes the conventional attitude in differentiating between grades of steel. He admits the desirability of high residual manganese for high-grade steels but fears that the added cost of such practice is not justifiable in the so-called commercial grades. It is granted that to charge high-manganese iron in order to obtain a 0.09 per cent. residual manganese is obviously ridiculous, but it is not granted that the procedure giving such results is faultless. Again, the additional cost of high-manganese iron is advanced as an argument against its use. To answer such an argument in full would necessitate a detailed analysis

TABLE 20

	No. Heats	Iron, Per Cent	Manganese, Per cent.	Iron from Ore, Per Cent.	Run-off Slag, Per Cent.	Limestone per Ton of Ingots	Residual Manganese	Residual Carbon
Pazetti.....	5	63.12	1.69	9.92	?	179	0.09	0.08
Chicago.....	34	59.47	1.72	8.13	26	238	0.21	0.116

	Total Iron	P <sub>2</sub> O <sub>5</sub>	MnO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> ·TiO <sub>2</sub>	CaO	MgO	Sulfur
Pazetti								
Run-off slag.....	27.06	2.13	14.57	23.56		17.47	5.04	0.12
Tapping slag.....	16.86	1.51	5.39	15.62		44.03	9.23	0.18
Chicago								
Run-off slag.....	22.81	2.04	14.01	23.19	2.38	20.81	7.67	0.08
Tapping slag.....	12.73	1.51	7.28	17.05	2.28	46.85	8.01	0.19

of blast-furnace operating costs which cannot be properly presented in this discussion. It is, however, my very definite conviction that in the main the cost of the two grades of iron would be the same. Briefly, the reasons for this opinion are as follows: The amount of manganese in excess of that naturally present in the iron which is derived from the iron ores used need not wholly be obtained from manganese ore, since there is available open-hearth slag which contains 9.08 per cent. manganese. This slag can be charged to the extent of 5 per cent. of the blast-furnace ore burden with no unfavorable results, and such practice will result in the production of an iron that will carry approximately 1.50 per cent. manganese if the usual iron contains 1 per cent. of this element. The additional manganese needed to reach 2 per cent. should be derived from those manganese ore deposits whose irregular or insufficient manganese content prohibits their use for any other purpose, and in consequence such ores should be obtainable at a cost but little higher than iron ore. Let it be assumed, however, that such ores are not obtainable and that one is forced to purchase 47 per cent. manganese ore for the purpose of raising the manganese content of the iron from 1.50 to 2 per cent., that such ore will cost \$33.86 per gross ton and that the utilization in the blast furnace is 60 per cent.; under these conditions, each ton of iron produced will require 39.7 lb. of 47 per cent. manganese ore, which will add 60 cents per ton to the cost of the iron and will result in an ingot cost of \$30.08

(based on corrected cost) per ton. I am convinced, however, that the cost of such a manganese ore addition would not be followed by an increased cost of iron in direct proportion to the quantity used, because when using an iron containing 2 per cent. manganese the steel works can without difficulty use an iron at least 15 points higher in sulfur content than when 1 per cent. manganese iron is employed. In consequence of this higher sulfur content, it should be possible for the blast furnace to reduce limestone burdens, slag volumes, and coke consumption and to increase production. The summation of such changes in practice might reasonably be expected to result in a decrease in the cost of such iron equivalent to 10 cents per ton. If such be the case, the cost of the 2 per cent. manganese iron will become \$28.50 per ton and the cost of ingots \$30.01, which is 22 cents less than the cost of the standard iron low-silica ore heat. Add to this 22 cents the profit incident to an unquestionably improved quality of steel and increased percentage of product at the rolling mills, and it is obvious that those works using 2 per cent. manganese iron will increase their earning power tremendously.

The suggestion that 35 per cent. iron charges of 0.75 per cent. silicon iron would fail to melt with sufficient carbon is again a product of unfavorable local conditions, for with fast-working furnaces of modern design and good producer gas, plus reasonable limestone burdens, such iron is both practical and desirable.

The heat charged with an iron of 1.75 per cent. silicon was shown (as stated in the text) to emphasize the excessive costs due to the use of such high-silicon irons, and the bases were increased proportionally and in the same ratio as used in all other heats except the excess limestone and are thus comparable in costs. Mr. Pazetti's statement that furnace linings suffer severely when working highly siliceous charges is correct; and when one is forced to work with such charges a part of the total limestone necessary should be charged in such a manner as to flux the acids of the slag before the furnace banks are attached. Such a procedure was in mind when the cost of the 1.75 per cent. silicon iron heat was calculated.

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## Absorption of Sulfur from Producer Gas in Open-hearth Furnaces

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(New York Meeting, February, 1924)

THE subject of this paper is one to which there are many references in the literature on the manufacture of steel in the open-hearth furnace, but few actual experimental data have been published. For that reason, the presentation of results obtained from two open-hearth heats where attempts were made to measure the sulfur absorption will be of considerable interest and value. The two heats on which the experiments were made were Armco ingot-iron heats and differ from the usual open-hearth heat of medium- or mild-carbon steel in that the refining is carried further; in this product the carbon and manganese are reduced practically to traces. In most other respects, and especially in respect to the absorption of sulfur from the producer gas, the two heats are typical of usual open-hearth practice.

The object of the experiments made on the first Armco iron heat was to determine the fluctuation of the composition of the metal bath and the slag throughout the course of the heat, with especial reference to the variations in sulfur. It was hoped to determine whether there was an increase in sulfur in the bath from the producer gas and if so at what stage in the process the increase occurred.

The experimental method consisted of charging analyzed scrap and pig iron, so that the sulfur in the charge could be calculated. Then, throughout the duration of the heat, metal and slag samples were taken every half hour, beginning as soon as there was enough molten metal to take a sample. These samples were analyzed; the results are given in Table 1. All domestic scrap was used and the charge was made up as follows:

HEAD END		FINISH	
	POUNDS		POUND
Pig iron.....	36,300	Pig iron.....	23,900
Sheet scrap bundles.....	36,200	Sheet bars.....	23,900
Sheet bars.....	40,200		

The total charge, exclusive of the re-pig added near the end of the heat, was 160,500 lb. The limestone charged was 21,400 lb., or 13½ per cent.

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\* Metallurgist, The American Rolling Mill Co.

A number of samples of the pig iron and the scrap used were taken for sulfur determination. The results of these samples are as follows:

Two samples of pig iron analyzed 0.030 and 0.032 per cent. sulfur; average 0.031 per cent.

Six samples, representing the sheet bars, gave 0.063, 0.059, 0.030, 0.031, 0.040, and 0.042 per cent. sulfur; average 0.044 per cent.

Four samples representing the sheet scrap showed 0.026, 0.033, 0.030, and 0.027 per cent. sulfur; average 0.029 per cent.

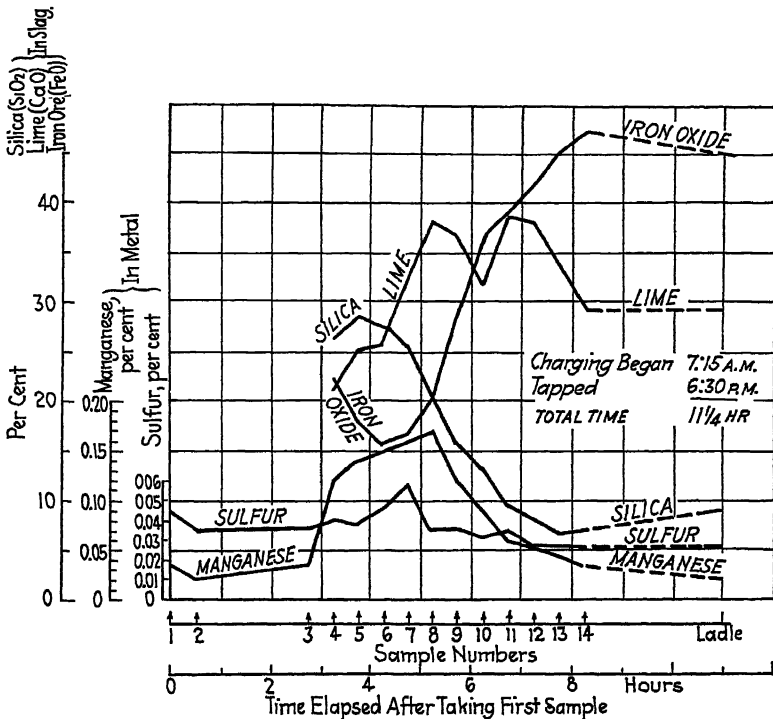


FIG. 1.—ANALYSIS OF SLAG AND METAL ON FIRST TEST HEAT.

Based on these figures the average sulfur in the charge was 0.036 per cent.

The charging of the head end began at 7:15 a.m., and the first metal test was taken at 10:00 a.m. and the second at 10:30 a.m., before the finish was charged. The third metal test was taken at 12:45 p.m. after the charging of the finish. At 1:15, metal and slag samples were taken—this was the earliest that a slag sample could be obtained. Metal and slag samples were then taken regularly at half-hour intervals thereafter. A record of the furnace operation and the additions made is given in Table 1 under Remarks. The heat was tapped at 6:30 p.m. and the

TABLE 1.—*Analytical Results and Data on First Armeo Iron Heat*

Sample Num-ber	Time When Taken	Metal Sample					Slag Sample							Remarks
		Per Cent. Sulfur	Per Cent. Phos- phorus	Per Cent. Carbon	Per Cent. Manganese	Per Cent. SiO <sub>2</sub>	Per Cent. FeO	Per Cent. CaO	Per Cent. MgO	Per Cent. MnO	Per Cent. Sulfur	Per Cent. P <sub>2</sub> O <sub>5</sub>	Per Cent. Total	
1	10:00 a.m.	0.044	0.080	0.085	0.085									Metal test only taken.
2	10:30	0.035	0.021	0.080	0.019									Metal test taken dolomite added to the banks at 10:32 a.m.; finish charged between 10:40 and 10:50; dolomite to front banks at 10:55.
3	12:45 p.m.	0.036	0.028	0.72	0.038									Metal test at 12:45; metal very thick.
4	1:15	0.040	0.032	0.39	0.12	26.34	23.32	21.28	9.62	15.48	0.09	0.78	95.91	Fourth test metal and slag taken.
5	1:45	0.038	0.029	0.52	0.14	28.42	17.71	25.20	9.99	15.77	0.10	0.62	97.81	Columnar black shiny crystalline; very few holes—almost solid; few white lime inclusions.
6	2:15	0.046	0.032	—	0.53	27.65	15.84	25.62	10.30	13.75	0.10	0.89	94.65	Columnar black shiny crystals, few blow holes; few lime inclusions at top.
7	2:45	0.058	0.026	0.50	0.16	25.57	16.56	32.34	7.06	11.24	0.12	1.35	94.24	Columnar black shiny crystals, larger crystals and more blow holes than number 4; few lime inclusions
8	3:15	0.035	0.029	0.34	0.17	20.20	20.30	38.36	4.95	9.05	0.14	1.61	94.61	Columnar black shiny crystals, few blow holes; few lime inclusions at top.
9	3:45	0.036	0.028	0.020	0.12	15.67	28.51	36.68	4.62	8.78	0.14	2.46	98.86	Black very spongy; lime inclusions in center.

10	4:15	0.032	0.007	0.011	0.09	13.11	36.72	31.64	6.04	7.76	0.16	1	40	96	83	Black and solid with center pipe; brittle, fell to pieces.	Tenth test metal and slag taken.
11	4:45	0.034	0.005	0.010	0.058	9.28	39.16	38.70	4.96	5.52	0.14	1.11	98	87		Black and solid except for spongy pipe.	Eleventh test metal and slag taken; heavy boil, carbon almost gone; dolomite manganese test at 5:00 p.m. showed manganese 0.042 per cent.
12	5:15	0.027	0.005	0.011	0.053	8.01	41.90	38.08	5.14	4.46	0.16	1.03	98	78		Columnar black very fine crystalline piped center.	Twelfth test metal and slag taken; 1500 lb. ore added; second laboratory test gave manganese 0.039 per cent.; 600 lb. pig added.
13	5:45	0	0.027	0.006	0.010	0.045	6.74	45.07	33.88	7.52	3.83	0.16	0.79	97	99	Black and solid except for spongy center.	Thirteenth test metal and slag taken; 1000 lb. ore and 400 lb. pig added.
14	6:15	0.027	0.004	0.010	0.034	7.06	47.08	29.40	5.10	3.65	0.15	0.76	93	20		Very similar to number 13.	Fourteenth test metal and slag taken.
Ladle.....		0.027	0.006	0.011	0.020	9.10	45.07	29.26	6.81	3.48	0.14	0.79	94	65		Black and spongy; this test taken from top of last ingot.	Tapped at 6:30 p.m.; ladle test taken after eighth ingot.

regular ladle test was taken after the eighth ingot; the ladle slag test was taken from the top of the last ingot. The metal in the molds had a normal appearance for ingot iron.

## DISCUSSION OF RESULTS

An examination of Table 1 reveals a number of interesting facts. The sulfur content of the metal samples, in general, increases up to the seventh test and thereafter falls to 0.027 per cent. at the end of the heat. This increase in sulfur during the melting-down stage amounts to 0.022 per cent.; that is, an increase from 0.036 per cent., estimated in the charge, to 0.058 per cent. on the seventh test. This increase in sulfur amounts to 0.44 lb. of sulfur per ton of steel. The probable source of this sulfur is the producer gas used in melting the charge, as this seems to be the only source from which such an amount of sulfur could come.

In our regular open-hearth practice, approximately 700 lb. of coal is used per ton of steel made. This coal is analyzed and contains not over 0.75 per cent. sulfur. Assuming a sulfur content of 0.66 per cent. in the coal and 300 lb. of coal per ton of metal used during the melting-down process, there would be 2 lb. of sulfur contained in the gas used for melting down. The

TABLE 2.—Analytical Results and Data on Second Armco Ingot Iron Heat

Sample Number	Time When Taken	Metal Sample					Slag Sample										Appearance of Slag	Remarks
		Per Cent. Sulfur	Per Cent. Phosphorus	Per Cent. Carbon	Per Cent. Manganese	Per Cent. SiO <sub>2</sub>	Per Cent. FeO	Per Cent. CaO	Per Cent. MgO	Per Cent. MnO	Per Cent. Sulfur	Per Cent. P <sub>2</sub> O <sub>5</sub>	Per Cent. Total					
1	2:50 p.m.	0.035	0.039	0.027	0.033											Sample taken from north door; hardly fluid enough to pour; metal test only; no slag.		
2	3:20	0.041	0.051	0.13	0.039											Metal test only; no slag.		
3	3:50	0.033	0.055	1.02	0.23											Metal test only from center door.		
4	5:30	0.050	0.077	1.64	0.15											Metal test only.		
5	6:00	0.045	0.057	0.81	0.10											Metal test taken; charge not all melted		
6	6:30	0.040	0.069	0.80	0.10	20.30	19.29	25.25	7.93	12.71	0.035	2.02	06.535	Black shiny columnar crystalline; few subcutaneous blowholes.		Metal and slag tests		
7	7:00	0.044	0.041	0.45	0.084	28.68	19.15	24.50	10.87	13.03	0.037	2.24	08.507	Similar to number 6.		Metal and slag tests; lime starting to come up at 7:15.		
8	7:30	0.041	0.033	0.26	0.092	27.23	18.57	25.76	11.76	12.54	0.042	2.38	08.202	Similar to number 7; smaller crystals		Metal and slag tests; unmelted metal still in bath		
9	8:00	0.045	0.026	0.10	0.12	25.96	16.56	31.22	9.08	11.77	0.042	2.52	07.152	Crystals have disappeared		Metal and slag tests; heavy boil; lime coming up fairly heavy.		
10	8:30	0.039	0.018	0.08	0.11	22.70	19.00	32.48	7.87	10.80	0.047	3.47	06.367	Similar to number 9; center not so spongy.		Metal and slag test; metal not yet under cover, dolomite to banks at 8:25; 300 lb pig at 8:50.		
11	9:00	0.046	0.016	0.025	0.11	21.63	19.20	36.12	6.60	9.82	0.060	4.02	07.48	Similar to number 9 and 10; large hollow in center.		Metal and slag tests; slag very thick.		
12	9:30	0.044	0.011	0.015	0.10	20.03	22.32	33.88	8.69	9.55	0.047	3.78	08.357	Black amorphous—more solid than number 11.		Metal and slag tests, 2500 lb ore added just after test; four pigs at 9:55		

13	10:00	0.043 0 006 0.015 0 064 12.50 41.32 26.22	5.01	7.80 0 080 2.12 94.58	Black almost nitreous; solid with hollow center.	Metal and slag tests; dolomite to banks at 10:10; two pigs at 10:25; metal not yet under cover.
14	10 30	0 043 0 006 0.012 0 042 11.40 38.58 33.18	3.16	7.56 0 084 2.16 94.404	Fine shiny black crystals; fine spongy center.	Metal and slag tests
15	11:00	0 033 0 008 0.012 0 042 8.98 37.87 37.52	6 22	4 64 0 100 1.95 97.280	Similar to number 14, more spongy.	Metal and slag tests, bowl at south end; dolomite on banks at 11:15, preliminary manganese, at 11:20
16	11:30	0.028 0.005 0.012 0 036 7 60 37.15 38.64	5 24	3.58 0 130 1.65 93.990	Solid but for small spongy center; fine crystals; no columnar structure.	Metal and slag test; a wound of unmelted metal still persists at center; eight pigs at 12:05
17	12:00	0 027 0 005 0.012 0 034 7 25 38.88 42.56	3.71	3 14 0 134 1 46 97.134	Similar to number 16.	Metal and slag tests; top hole flaming badly.
18	12:30 a.m.	0.028 0 005 0.012 0 025 7 10 37.00 43.40	6 53	3 07 0 135 1 31 97 545	Similar to number 16.	Metal and slag tests; metal under cover after eighteenth test; nine pigs at 12:45
19	1:00	0.027 0 005 0.012 0 025 6 90 40.75 38.82	6 22	2.62 0 163 1 59 97 063	Similar to number 16.	Metal and slag tests; eleven pigs at 1:15
20	1:30	0.028 0.005 0.012 0 031 6 60 40.60 38 92	6.04	2 62 0 125 1 41 96 315	Similar to number 16.	Metal and slag tests, temperature test at 1:40; sharp cut; metal out at 2:00; smoky in runner.
Ladle.....		0.029 0.005 0 012 0 023 13.98 39 31 33.74	5 79	2.19 0 087 2.08 97 177	Average of four samples on metal test.	

analytical results showed an absorption of 0.44 lb. of sulfur per ton of steel, which is 22 per cent. of the sulfur contained in the gas from 300 lb. of coal. The drop in sulfur after the seventh test coincided with the time when the lime was coming up heavy in the bath; the lime content of the slag increased from 25.62 per cent. at the sixth test to 38.36 per cent. at the eighth test.

The sulfur content of the slag increases from 0.09 per cent., in the fourth test, to 0.14 per cent., in the eighth test, and 0.16 per cent., in the tenth. There was a large increase in the amount of slag after the seventh test, caused by the lime coming up and the addition of 3000 lb. of iron ore. This increase in slag volume accounted for the large drop in sulfur in the metal without a correspondingly large increase in the percentage of sulfur in the slag. The amount of sulfur remains about the same and the slag volume is increasing, which means that the total amount of sulfur in the slag is increasing.

It will be noted also that the  $P_2O_5$  content of the slag increases to a maximum at the ninth test and then decreases; this is accounted for only by the increase in the slag volume. The dephosphorization was practically completed by the time the tenth test was taken, so that subsequent increase in slag volume decreased the percentage of  $P_2O_5$ .

Attention is called to the gradual decrease in  $SiO_2$  in the slag and the gradual increase in  $FeO$ . The  $CaO$  increases, until the eighth test, while the lime is coming up, and then remains fairly constant, except for test number 10, until the last few tests, where the  $CaO$  content decreases because of increase in  $FeO$  content. Notes on the physical appearance of the slag are given in Table 1.

## CONCLUSIONS

The principal conclusions to be drawn from the data obtained in this experiment are relative to the absorption of sulfur:

1. Large quantities of sulfur, possibly up to 0.025 per cent. or more, are absorbed from the producer gas by the charge in the open-hearth furnace during the melting-down stage; this is in addition to the sulfur already contained in the metal charged.

2. This sulfur absorption imposes a greater burden of desulfurization on the slag than would exist if a lower sulfur fuel were used.

## SECOND ARMCO INGOT IRON HEAT

The object of the second test was to verify the results obtained on the first, especially in reference to the fluctuations in sulfur in the bath.

The experimental method was the same; it consisted of charging analyzed scrap so that the sulfur in the charge could be calculated, then

taking slag and metal samples at half-hour intervals throughout the duration of the heat, and later analyzing these. The analytical results are given in Table 2. All domestic scrap was used and the charge was made up as follows:

HEAD END	POUNDS	FINISH	POUNDS
Pig iron.....	36,900	Pig iron.....	28,200
Sheet bars.....	52,000	Sheet bars.....	13,900
Sheet scrap..	9,100		
Sheet bundles...	40,100		

The total charge, exclusive of the re-pig, was 180,200 lb.; the limestone charged was 25,100 lb., or nearly 14 per cent. The sulfur in the charge,

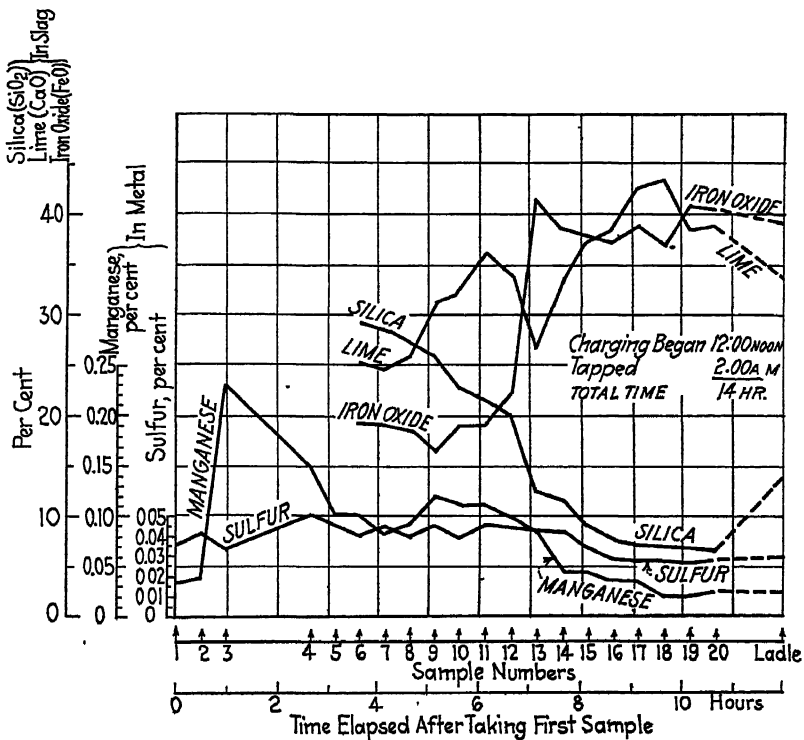


FIG. 2.—ANALYSIS OF SLAG AND METAL ON SECOND TEST HEAT.

estimated to 0.031 per cent., based on the analysis of the scrap charged was as follows:

					AVERAGE
Three samples of pig iron.....	0.031	0.023	0.025		0.026
Two samples of sheet scrap.....	0.028	0.030			0.029
Four samples of sheet bars.....	0.029	0.025	0.025	0.050	0.032
Four samples of sheet scrap bundles.	0.031	0.028	0.036	0.050	0.036



Charging of the head end began at 12 noon and finished at 12:45 p.m. The first metal test was taken at 2:50 p.m. and a second metal test was taken at 3:20. A third test was taken at 3:50 p.m. and the "finish" was charged at 4:00. The next sample was taken at 5:00. Table 2 gives the full notes and analytical results. The heat was regular for Armco ingot iron in every way, except that tests were taken every half hour. The furnace operation was normal.

Examination of Table 2 shows that the data are, in general, corroborative of that obtained on the first heat. The sulfur increases to a maximum on the fourth test but remains almost at this peak for several hours. The outstanding fact, however, is that the sulfur has increased during the melting-down period from 0.015 to 0.020 per cent. over the sulfur contained in the charge. And there is no source from which this sulfur could come but the producer gas.

It will be noted that the phosphorus builds up during the first four tests; this is accounted for by the pig iron melting first and so raising the phosphorus. The behavior of the carbon and manganese corroborate this.

The slag analyses conform, in general, to what was to be expected. The percentage of  $\text{SiO}_2$  drops progressively and the  $\text{FeO}$  and the  $\text{CaO}$  behave as was to be expected from the "coming up" of the lime and the iron-ore additions that were made. The sulfur in the slag increases from 0.035 per cent., on the first slag test taken at 6:30 p.m., to 0.163 per cent. on the nineteenth test.

The conclusions from this experiment are entirely corroborative of those of the previous experiment.

## DISCUSSION

GEORGE B. WATERHOUSE,\* Cambridge, Mass.—The users of fuel oil are alive to this question. In one plant where they use a low-sulfur fuel oil for the melting-down stage (naturally a more expensive oil), they use the lower cost high-sulfur fuel oil when the bath is melted and covered with the slag.

J. V. W. REYNDERS, New York, N. Y.—That, I believe, is the usual practice where the two grades of oil are available.

C. L. KINNEY, JR.,† South Chicago, Ill.—In evaluating coal, a great deal of attention is sometimes paid to the sulfur content alone. I would prefer to work with coal carrying a sulfur content of, say, 1.25 per cent., provided that coal carried 14,000 B.t.u., than with a coal which carried

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\* Professor of Metallurgy, Massachusetts Institute of Technology

† Superintendent Open Hearth No. 1, Illinois Steel Co.

0.75 per cent. sulfur but only carried 11,000 B.t.u., because we burn less coal, in all cases, with the higher B.t.u. coal, and get a higher flame temperature; the heats are made more rapidly, and under such conditions one can reduce, with the higher sulfur coal and the higher B.t.u., the sulfur content in the steel, compared with the other coal, from 10 to 15 points.

## Requirements of Refractories for Open Hearth\*

By F. W. DAVIS,† LINCOLN, NEB., AND G. A. BOLE,‡ COLUMBUS, OHIO

(New York Meeting, February, 1924)

THE purpose of this paper is not to report, to the Institute, the results so far obtained in the survey, by the Bureau of Mines, of the metallurgical requirements for open-hearth refractories, but to present an outline that we hope will serve as a basis for discussion.

The systematic survey that the Bureau proposes to make has not been outlined, although considerable preliminary work has been done in the way of interviewing open-hearth superintendents in several of the larger steel plants from the Chicago district eastward.

At the several conferences so many of the opinions were diametrically opposite, when considering the same point, that it was thought that such an opportunity as the Institute offers in the way of a clearing house for moot metallurgical topics should not be overlooked. For this reason, the paper has been prepared as a basis for a discussion which, it is believed, will be of value in outlining the program of the Bureau.

D. A. LYON,  
Assistant Director.

THE importance of securing suitable refractories for metallurgical operations is daily becoming more universally recognized; particularly in the manufacture of open-hearth steel, where the life and earning power of the furnace depends largely on the judgment and care exercised in the selection of the correct quality of refractory for each of the parts. Any innovation that would make available to the steel manufacturers refractories with longer life or better suited to their needs than those now employed, and at a cost that would permit of their use, would be of enormous value to the industry at large. It is quite probable that revolutionary changes would not be necessary. Material now used in some parts of the furnace might, by more suitable preparation, be made of much greater service; in other parts, possibly entirely different material would be necessary in order to effect much improvement.

Inasmuch as different parts of the furnace structure perform different functions and are subjected to different service conditions, a refractory suitable for one part will be entirely unsuited for another. For this reason, to make a comprehensive study of the refractory requirements of the processes, we should consider the furnace as built up of a number

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of refractory units and study the service conditions and requirements of each unit separately. In making this study, it would be well to approach the question with two objectives in view: (1) To obtain a refractory that will not only resist present conditions more effectively, but will, if possible, permit of higher temperatures being employed inasmuch as higher temperatures will increase production and lower costs far in excess of the actual temperature ratio; (2) As the thermal efficiency of the open-hearth furnace is rarely over 17 per cent. and as about 65 per cent. of the total heat loss is accounted for by radiation and conduction, the possibility of obtaining refractory materials of lower thermal conductivity than those now used, or of such nature as to permit of their being supplemented by a heat insulator, should be investigated. In either case the operator would be able to conserve a greater proportion of his total heat for useful work than is possible with present equipment.

The A. S. T. M. has tentatively listed the properties that a refractory should have for any service. The five major properties are the ability to withstand: temperature, load, spalling, slag, abrasion. The fact that all these properties will not have to be emphasized in any but a very few services is taken into account.

There are other properties, however, that a refractory must have in certain cases; in fact, any of the following may assume major importance in a refractory for certain furnace parts: slaking in moist air, permanent volume change, vitrification range, heat conductivity, thermal expansion.

A committee of the Refractory Manufacturers Association is now working on the service requirements for refractories. When this work is completed, it is hoped that it will be possible for the consumers of refractories to order their ware by a service number, which will designate the service to which a given refractory is suited.

### THE FURNACE

For our study, the open-hearth furnace will be divided into the following units, which will receive individual attention: hearth, bulkheads, roof, side walls, ports, uptakes and slag pockets, regenerators. Before dealing with the specific requirements of the various parts of the furnace, however, it would be well to state briefly certain fundamental properties essential to all open-hearth refractories. A refractory should have no permanent shrinkage; this factor is of greatest importance in arch brick, although in any case, where a gas-tight wall is desired, it cannot be overemphasized. It is essential that the refractories do not slake when cold and exposed to atmospheric air; in present practice, some dolomite bottoms have this tendency, and while it is a very undesirable property, it is easier to guard against it in the bottom of the furnace than in many other parts, where it might prove ruinous. These requirements are so

fundamental as to be taken for granted; however, when selecting an entirely new material they must be considered.

### *Hearth Section*

Magnesite is the material most favored by operators for hearth construction. For this purpose a mixture containing about 75 per cent. calcined magnesite and 25 per cent. basic slag is applied in layers, each layer being sintered in place. Dolomite has been used instead of magnesite, but does not give as good service.

Any material used for the hearth of the basic furnace must be of a basic nature in order to resist the action of the furnace slag. It must permit of a dense structure being built that will be impervious to the passage of molten steel and slag at furnace temperatures. To attain this condition, a refractory with a long range of vitrification is required; one that will frit together without undue softening. The resistance of the hearth both to load and mechanical shock must be high; this section of the furnace not only supports the weight of the metal and slag, but is subjected to considerable mechanical shock when the furnace is being charged. A material that would fail or crack under this service would be totally unsuitable.

The formation of pockets or holes in the hearth constitutes the chief difficulty encountered in this section. This trouble, in many cases, is probably caused by some defect in the original sintering, although it might be attributed either to excessive spalling, occasioned during charging cold material, or to small cracks formed through mechanical shock.

Records show that chrome has been used as a material for hearth construction, with apparently no improvement over magnesite; bauxite has also been used for this purpose. From all information obtained, however, it is concluded that magnesite is probably the best hearth material in sight.

### *Bulkheads*

The bulkheads of the furnace are, in reality, a continuation of the hearth, extending to the lower port, and are constructed as a part of the hearth, but the service conditions differ considerably from those of the hearth. It is not so essential that the bulkheads resist load or mechanical shock conditions; they will, however, be subjected to a greater slagging action and part of their surface is exposed to the direct flame action as well as to considerable mechanical abrasion by the suspended particles in the gas. While magnesite gives more satisfactory results than any material so far used for the bulkheads, a material that would resist the combined slagging, abrasive, and flame action to a greater extent would be highly desirable.

### *Roof*

Silica is used almost universally in the roof of the open hearth. Its chemical character, as well as some of its physical characteristics, are not suited to the service. Its low cost, together with two favorable physical properties, has favored its use. Silica refractories will stand up under load to a temperature only slightly below their melting point. The relatively high thermal conductivity enables heat to be drawn away from the region just back of the fused surface so fast that the main body of the shape is much below its softening temperature. While this latter property is necessary in order to allow this type of refractory to hold up in spite of its relatively low softening temperature, it is undesirable in the ideal refractory for this service in that it brings about large heat losses. The ideal refractory should have a low heat conductivity or be so refractory as to permit of insulation. The fact that silica undergoes isotropic changes that are accompanied by large volume changes renders it unfit for this service unless great care is taken when heating up and cooling down the furnace.

The atmosphere of the open-hearth furnace is heavily charged with oxide vapors from the bath as well as slag splashes. In addition, the gas will, from time to time, contain appreciable quantities of pulverized lime and fluorspar. Little information is available as to the physical characteristics of these vapors and dusts, such as size, hardness, and velocity of particles; however, they are known to be of a basic nature. Silica, being an acid material, will not resist the action of this basic dust and vapor; therefore, from a chemical standpoint, silica is not the correct roof material.

To make any definite statement as to the exact requirement for roof material would, in view of our limited knowledge of all conditions to which the roof is subjected, be rather premature; however, in a general way, we might state that a refractory for this service should be capable of maintaining an arch under temperatures approaching 3400° F., and that it should be of a basic nature.

### *Side Walls*

The side walls of the furnace, like the roof, are constructed of silica brick and are subjected to somewhat similar service conditions. The necessity for mechanical strength at operating temperatures is not so great as with the roof brick; but, on the other hand, the side walls are exposed, at times, to the direct action of the basic slag.

In many furnaces, a course of neutral brick is laid between the hearth and the silica of the side walls. This neutral material tends to prevent any chemical action between the acid wall and the basic hearth and gives the wall some protection from the basic slag; however, even with this

protection, the side walls, as well as the roof, to be chemically correct, should be of a basic nature.

There are several instances on record where the back wall of the furnace has been built of chrome brick; varying success has been reported, but little information has been published except by the producers of this material. Magnesite has not been found suitable for this service because of its inability to carry loads at high temperatures. Both magnesite and chrome have a decided tendency to spall when subjected to sudden heat changes, which tendency would further indicate that these materials will probably not be the ideal refractory for this service.

### *Ports*

The port system, which, taken as a whole, constitutes the burner, is the most sensitive part and the one that governs, to a large extent, the proper operation of the open-hearth furnace. For this reason, a port that will stay put, so to speak, would be of great value to the industry.

The ports are built at each end of the furnace and so constructed as to direct the streams of gas and air to impinge very slightly on the bath and away from the roof. The stream of air, being uppermost, adds some protection to the roof by further depressing the gas stream; the direction of the streams is so arranged as to cause a mixing of the two for combustion. Any change in dimensions of the port, caused by slagging away of the brick, will affect materially both the mixing of the gas and air and the protection given the roof; it may also cause the flame to impinge directly on the bath and effect excess oxidation therein.

The wall separating the gas and air ports, which is, in reality, an arch over the gas port, is constructed of silica brick and protected to some extent by water cooling. This water cooling, while it lengthens the life of the port, is not the ideal arrangement inasmuch as it tends to carry heat away from the gases immediately prior to combustion, thereby decreasing the heat of the furnace at the point where high temperature is most desirable. Because of the intense heat to which it is subjected, and in order to protect the silica brick from the basic slag and dust, the bottom of the gas port is usually protected by a layer of magnesite or chrome.

Four of the five major points charted by the A. S. T. M are of prime importance in this service; they are: temperature, load, slag, and abrasion.

The heat, slag, and abrasive conditions at the arch and in the port, in general, are so severe that no refractory now in common use has given satisfactory results. While temperatures above 3200° F. are uncommon, it would be desirable to be able to raise this limit 200°. Neither chrome nor magnesite shapes are suitable for arch material as they will not support an arch at the temperatures obtained in the ports, although their

chemical character is correct. Carborundum bricks have been tried, but are not satisfactory because the carbide tends to decompose, especially under the oxidizing conditions of the open hearth. Spinel and sillimanite have been tried in one or two cases and appear to have possibilities. Much work must yet be done before the ideal refractory for this part of the furnace is developed.

### *Uptakes and Slag Pockets*

The uptakes of the open-hearth furnace are the vertical flues that connect the ports with the slag pockets. These are chambers at the base of the uptakes that catch and retain any solid matter carried over in the products of combustion and prevent its entrance into the regenerators. Both uptakes and slag pockets are constructed mainly of silica brick, although in some cases, some magnesite brick is inserted in the upper lining of the uptakes, directly behind the port.

The products of combustion enter the uptakes at temperatures from 2800° to 3000° F. and are heavily laden with vapor, dust and finely divided slag. The vapor probably consists of metallic oxides; the dust may be from any material used in the process; the slag is, of course, basic. The brickwork will, therefore, be subjected not only to high temperatures but to considerable slagging and mechanical abrasion at these temperatures. On the half of the cycle when gas is being burned at the port, the gas uptake will conduct a highly reducing gas at about 2000° F., and the air uptake will carry air at about 2300° F. The reducing effect of the hot gas must not be overlooked when selecting a refractory for this purpose.

So far as ability to carry load and maintain an arch at the indicated temperatures is concerned, silica is suited to the service, but where the temperatures are highest, the fluxing and abrasive actions of the basic slag are excessive. Here, as in the side walls and roof, the use of a basic refractory is indicated. As hard-burned material as is consistent with resistance to spalling should be used to prevent penetration of gases and dust with subsequent fusion. The refractory should be of such nature as to permit its being supplemented by heat-insulating material in order to prevent excessive heat losses.

### *Regenerators*

The regenerators of an open-hearth furnace function by absorbing the sensible heat from the escaping products of combustion in one part of the cycle and delivering the heat to the incoming air and producer gas in the other part. In furnaces using natural gas, coke-oven gas, tar, oil, or powdered coal, the regenerators are used to preheat the air only.



Essentially, the regenerators consist of two brick chambers at each end of the furnace filled with checker brick or tile, arranged in such fashion that they will absorb the maximum amount of heat and, at the same time, not retard the draft unduly.

In practice, the regenerators will receive gases of combustion at temperatures around 2600° to 2800° F., cool them to about 1200° F., and, on the other part of the cycle, will receive producer gas at about 1100° F., air at atmospheric temperatures, and heat both to from 2000° to 2300° F. These temperatures, of course, will vary over a wide range, according to the individual practice.

The fireclay refractories now used in the regenerators appear to be well suited for the purpose for which they are intended; *viz.*, the absorption and emission of heat. The temperature demands are well within fireclay service. There is little tendency to spall even when the checkers are cleaned. In this service abrasion is of minor importance. The clays will carry the load to which they are subjected safely at service temperatures. It is highly desirable, however, that a checker brick shall not collect slag and carbon or attain a glassy surface by fluxing with the flue dusts, as all of these factors will reduce its efficiency in the absorption and emission of heat. It is also desirable that the brick contain a minimum amount of oxides of iron; any oxides of iron will be reduced by the action of the hot producer gas, resulting in the ultimate destruction of the brick.

An ideal refractory for checker brick will be one quite similar to fireclay brick now used except that it should have a minimum slagging action with the flue dirt, and that it should be relatively free from iron. Washed fireclays have been used in the manufacture of checker shapes and have been reported to give longer life than shapes made from the same clay unwashed.

### DISCUSSION

Three of the more important points that, of necessity, will determine the lines along which future research will develop are: (1) The relation between the service and the allowable cost of a refractory; (2) the ideal relation of the life of the individual parts to the life of the furnace; (3) the exact conditions under which a refractory must serve.

### Cost

It would appear that for a commodity so essential to metallurgical operation as refractories there must exist a rather definite relation between service and allowable cost. The several men interviewed, however, had wide differences of opinion. One operator thought that a refractory that would double the life of a roof could demand five times the price now being paid. A purchasing agent thought that the

plant could probably stand three times the cost of the ware now in use. A consulting engineer said that a refractory should give service in direct proportion to its selling price. One person said that a refractory that would cost twice the price now being paid should give three times the service.

The cost of a refractory will be more or less determined by the location and abundance of the raw material used, together with the amount and cost of preparation necessary to produce the finished product. The common refractories, such as fireclay and silica brick, are ordinarily made from abundant materials secured locally and by ordinary quarry or mining practice. No beneficiation is necessary; the crushing, grinding, and tempering are simple; the shapes are machine or hand made, but in either case the cost of fabrication is low, drying is not difficult nor expensive. This type of refractory is fired but once at a moderately high temperature.

Chrome refractories belong to the once-fired type, but the raw material is brought from remote parts of the globe and is relatively scarce. Magnesite not only must stand a high transportation cost, but an importation duty. The raw material is calcined to a high temperature before being made into shapes. Both chrome and magnesite, in this country, owe a part of their high cost to the fact that they are burned in periodic kilns in which they must be protected by two and one half times as many burned silica brick. These brick must, of course, be heated to the kiln temperature at each burn, necessitating an abnormally high fuel consumption. The frequent heating and cooling of the silica will further result in a high percentage of breakage.

The raw materials for refractories, such as bauxite and zirconia, occur in limited amounts and are located far from the centers of consumption. These refractories have a high residual shrinkage when burned at the ordinary temperatures used in ceramic kilns. A sintering or fusion of the raw material is desirable before forming the ware into shapes; the bonded sinter should be burned at a high temperature.

Refractories, such as synthetic sillimanite, spinel, corundum and carborundum, which may possibly fill a limited demand where an especially heavy service is indicated, are electrically fused and in many cases are reburned at electric furnace temperatures after being made into shapes. To what extent, if any, the manufacturing cost of such refractories as sillimanite, spinel, and corundum can be reduced by the utilization of the natural mineral depends on the locating of economic deposits of these ores, and on the cost of transportation and beneficiation.

Whether any marked saving can be made by placing unburned refractory shapes in a furnace is worthy of investigation. Cobbed chrome ore is reported to have been so used successfully in back walls; also, calcined magnesite in metal containers has given good service. The fluxing

and burning of silica to produce a tridymite brick appears to offer promising possibilities.

With these production considerations in mind it is evident that some idea as to the price which the trade could well afford to pay for a refractory material would be a valuable guide to any future research.

### *Life*

The second major point on which agreement does not seem to be general has to do with the utility of increasing the life of one part of the furnace unless it be possible to increase the life of all parts to a corresponding degree. Some operators think that if a furnace could be so constructed, and the life of all parts of the furnace so regulated that it would reach its limit of service, as a whole, we would have the ideal condition. Others are convinced that this view is fundamentally wrong, their idea being that a furnace is inevitably slowed down gradually in certain parts—as by the clogging of checkers, slagging and erosion of ports, etc.—and that repairs can be more economically made while the main body of the furnace is in fairly good shape.

### *Service Conditions*

The conditions to which a refractory will be exposed in service must receive primary consideration when making a selection. Certain of these conditions are known and have been previously cited; but there are many important points on which different operators disagree and still others on which sufficient data are not available on which to base even an estimate.

The temperatures to which refractories are subjected have a great bearing on the service they will give. Various authorities have quoted certain furnace temperatures, but an examination of these data shows that the values vary over a wide range. No doubt this apparent discrepancy is the result largely of differences in operating conditions. Assuming that different operating conditions will be accompanied by differences in temperatures, we find that there is need of a great number of temperature observations covering, if possible, all practices and conditions. In collecting these data, the temperatures of the furnace atmosphere at all points of the furnace, as well as the refractory surfaces, should be taken.

Another service condition of which little is known is that of furnace atmosphere. Inasmuch as the open-hearth process is essentially an oxidizing process, the atmosphere over the bath must, of necessity, be oxidizing. However, the nature of the film of gas in contact with the roof is not known. We should have reliable data regarding the nature of the gas at all parts of the furnace and during all stages of the operation.

In certain parts of the furnace, the refractories are damaged by the action of the vapor or dust content of the gas. This damage is accomplished either by chemical action or abrasion or a combination of both. The average operator's idea of this material suspended in the furnace atmosphere is somewhat indefinite. It has been described as a mist rising from the bath, or as a dust from the charges; it is of great importance to have exact information regarding this material, whether it is a vapor, a dust, or a combination of both. We should also know the chemical composition and quantity of this material as well as other data, such as size and hardness of particles, and some idea of the velocity at which they strike the refractory surface.

## DISCUSSION

C. L. KINNEY, JR.\* South Chicago, Ill.—The evaluation of a better refractory presents certain difficulties, because of its varied characteristics or varied life in different parts of the furnace. Nor do any of us know what results would follow the use or application of a refractory that would enable us to neutralize the large heat losses through the roofs and the side walls surrounding the melting chamber and the effect of neutralizing these losses on the increase in flame temperature. From a practical standpoint, that is an unexplored region. Nor is it generally taken into consideration as to what portion of the lost time due to failure of refractories should be applied to the purchase or the higher purchase price of better grade refractories.

To take a specific case. If we assume that under average operating conditions a silica roof will run for 325 heats but during that period it becomes necessary to replace a back wall, there is involved in each of the replacements not only the labor and material but also the potential tonnage lost. How and in what manner shall we evaluate that lost tonnage and what proportion of the money loss shall we apply to the securing of a better refractory?

From a practical standpoint, although perhaps not a financial one, if a furnace will produce steel at the rate of 6 tons per hour and it takes 4 hours to replace a back wall and to get the furnace back to melting temperature again, each replacement will represent the loss of 24 tons of ingots. Then the problem is to decide what that 24 tons of ingots may be worth. If that 24 tons of ingots will represent 75 per cent. of shippable product from the mill dock, knowing what the net profit to the company is on that 75 per cent., it becomes relatively simple to apply the money lost by these excessive shutdowns to the purchase price of better refractories.

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\* Superintendent of Open Hearth No. 1, Illinois Steel Co.

Evaluating certain refractories in that manner seems to indicate that we are paying perhaps too high a price, in this specific case, for such materials as magnesite and chrome brick. The combustion chamber and the port ends of the furnace are those parts that need more suitable refractories. The roof, in particular, is an attractive proposition. The back walls, the bulkheads, and the end walls of the furnace, by their early failure and by excessive accumulations of slag in the slag pockets, tend to terminate the effective campaign of the furnace much earlier than it should be.

But underlying it all is the fact that we want a refractory and probably can afford to pay, in certain definite locations in the furnace, a price far in excess of what we are now paying for silica, magnesite, and chrome brick.

I cannot see where there is much hope of improving silica brick to a point where we can get the extraordinarily high flame temperatures that the process is ultimately going to demand. Silica brick, in a neutral atmosphere, has a fusion point of  $3100^{\circ}$  or  $3150^{\circ}$  and if the presence of oxides, lime dust, and various other fluxing materials are considered, you will realize it would not be unfair to assume that that  $3150^{\circ}$ , in service perhaps comes down to  $2950^{\circ}$ .

If flame temperatures, when burning producer gas in the furnace, are observed, they will be found run about  $3400^{\circ}$ ,  $3450^{\circ}$ , and, in some cases,  $3500^{\circ}$  F. It is obvious under such conditions that arrangements must be made to inject the flame into the furnace in such a fashion that the solid-fuel column cannot come in contact with any of the surrounding fractures; and if the fuel column does, or even stray portions of it, come in contact, there follows an immediate fluxing of the brick. That is followed, in practice, by an attempt to raise roofs and by various other devices to keep the flame away from the side walls and roof. Sometimes keeping the flame away from the roof is accomplished by using excessive quantities of air, which reduces the flame temperatures.

If we could find a material with a fusion point somewhat above that of our practical flame temperatures we would be able to carry these temperatures to a higher point and the resultant increase in production would enable us to pay for such material a price that we would now consider out of the question.

It is a common practice now to water-cool the ports, which occasions considerable loss of combustion efficiency. It is not necessary to use high-priced basic materials in the lower portion of the furnace; the checkerwork, in general, stands up nicely and performs its functions well.

L. F. REINARTZ,\* Middletown, Ohio.—When it comes to discussing the cost of refractories in open-hearth operations, great stress must be

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laid on the time saved when more expensive refractories are used because of decreased number of minor repairs throughout the run or campaign of a furnace. Often the initial cost of a refractory is not so important as the relative length of time it will resist the wear in a furnace compared to a cheaper grade of refractory.

We have estimated that it costs \$50 per hour to shut down an open-hearth furnace for small repairs during the life of the furnace. If an entire backwall must be replaced, which normally causes about 4 hours delay, this repair has cost the department \$200 plus the actual cost of labor and material. In our operations, we know that we are justified in paying more than three times the original price for a refractory if we can be assured of twice the life.

Recently, I saw several backwalls laid up with chrome-ore blocks instead of silica brick. I was told these walls cost at least three times as much as the silica walls, but some of them have made 175 heats before requiring a patch. Decreased number of delays on an open-hearth furnace result in better operations all along the line, which can also be capitalized indirectly. Mill schedules can be more accurately controlled; number of "soaker heats" can be cut down; furnace brickwork throughout the furnace, especially the roof, will show longer life due to less sudden expansions and contractions in the same.

I doubt if it will be possible to build an open-hearth furnace that will fail all over at the same time. Improvement in open-hearth practice for years has gone along in a seesaw fashion. When one weak point was strengthened, another showed up. The gradual trend of the industry, nevertheless, has shown good results as far as increase of yearly tonnage is concerned. I believe the present tendency is to improve the port and superstructure construction of an open-hearth furnace so that during a run it will be possible to shut down a furnace temporarily, cut the slag out of slag pockets, and clean the soot out of the checker chambers rapidly by improved methods, so that a furnace may deliver *maximum* tonnage throughout the run, and the furnaceman may have proper control over reactions.

In our particular business, making ingot iron, a factor that influences the life of our refractories is the corrosive action of the furnace gases, which are heavily laden with iron-oxide fumes during the latter part of every heat. The usual technical investigator often fails to take this factor sufficiently into consideration, and therefore it is difficult for him to understand why a brick that shows very good physical tests and high fusing point does not give the expected results in the furnace. The lower carbon the steel that is made in an open-hearth furnace the more severe is this action on front and back walls, roofs, ports, etc. Slag pockets are rapidly filled with a dense oxide of iron slag. It penetrates the brickwork when a furnace is new and, in time, lowers the melting

point. Large quantities of iron oxide lodge in the checker chambers, and cause them to clog up very rapidly.

Often these deposits are erroneously called "carbon" deposits. Many tests have shown that no carbon is ever found in such accumulations, either in the gas or the air checkers. Recently, we weighed all the deposit in a set of checker chambers after a run of 150 heats on a cold-metal practice and found that 70,000 lb. of soot had been deposited, or about 0.25 per cent. of every charge went over into the checkers as dust. This deposit was very high in iron oxide and often ran over 2 per cent. in sulfur. When this amount of iron is added to the iron in the slag in the slag pockets, the iron absorbed in the brickwork, and the iron going out of the stack as fumes, we can have a better idea why the metallurgical loss in making extremely low-carbon metal is so high.

One point brought out by the investigators in reference to the corrosion of furnace bottoms indicated that they believed holes in the bottom of a furnace were often caused primarily by mechanical shock, possibly during the charging period. I do not believe much bottom trouble comes from this source, because a magnesite bottom, at furnace temperatures, is extremely tough. In most instances, such bottom trouble comes from absorption of iron by the magnesite, which lowers its resistance to high temperature reactions. At other times, furnace helpers may not be as careful as they should be to drain all the metal out of a furnace while tapping the heat; this metal then becomes mixed with the limestone and bottom material. During the working of some succeeding heat, the furnace helper may allow the metal in the furnace to become too hot, or the heat may melt high in carbon; in either case the familiar boil may start on the bottom toward the end of the heat. The damage done to the bottom will then be dependent on the length of time it continues and the skill of the furnace man. In any case, if a bad hole has been torn in the bottom, it pays to wash out the furnace thoroughly with spar and river sand, being sure to allow all such additions to run out of the tap hole. It is often necessary to cut the tap hole down quite a distance to allow all metal to drain out. If a good patch is then burned into the bottom with Austrian magnesite, no trouble will be experienced with that place for a long time.

Careful attention on the part of a melter to see that bottoms are drained dry after every heat, that lime is not allowed to accumulate in the bottom, and that heats are not worked down at too high temperature will go a long way to help prevent bottom troubles.

Labor conditions are becoming more acute each year. Furnace helpers must often be trained in a very short time. In the next generation, open-hearth furnaces are going to be run in a more scientific manner. The blast-furnace men have, for many years, had a better knowledge of exact conditions in every part of furnace than we have in the open-

hearth operation. We have still many things to learn about an open-hearth furnace, which will ultimately help us make more tonnage, and better quality.

In a producer-gas fired furnace we should know the temperature and pressure of the gas leaving the gas producer. We should have an automatic CO<sub>2</sub> recorder to tell something of the quality of the gas. The reversing valves should not be controlled by the whim of a first helper nor by any arbitrary time limit, but should be reversed as the checker chambers and furnace require. That means a pyrometric system in the checker chambers that will be efficient; it also means a type of valve that can be adjusted to various checker-chamber conditions, which means independent regulation of valves. Every stack should be equipped with draft gage, pyrometer, and recording CO<sub>2</sub> device. Such control, when once worked out, will save coal in gas producers, furnish better gas to the furnace, increase tonnage, cut down refractory and lost time cost, and make better quality control in furnace possible.

The Bureau of Mines can be of great assistance to practical furnace men if it will help devise some refractory material that can be used for the purpose of taking temperatures of the metal in a bath by means of a high-temperature pyrometer.

P. E. McKINNEY, Washington, D. C. (written discussion).—When discussing production of steel from a standpoint of quality, which involves leaving the steel in the furnace until it has reached its proper degree of refinement, regardless of time involved, the question of selection of refractories becomes an important factor, and those refractories that make up the hearth must be selected with the most painstaking discrimination.

Probably the most serious hearth trouble is experienced with the basic electric furnace. In preparing a furnace hearth for this process, magnesite bricks are used, upon which a hearth is built from dolomite or magnesite bonded with fusible material, such as basic slag or iron oxide, which will permit sintering to a vitreous condition at moderately high temperatures. As the average electric furnace cannot use oil or gas flame for sintering the hearth, this is done by burning in the initial bottom, by placing a block of carbon on the furnace bottom and effecting an electrical contact between the electrodes of the furnace. Repairs to the hearth between heats are made by filling the cavities in the hearth with the magnesite or dolomite mixture immediately after the heat is tapped and depending on the radiated heat from the roof and walls of the furnace to effect sintering. To obtain these properties of long sintering at moderately high temperatures the percentage of fluxing elements in the refractory must be fairly high; in practice these fluxing elements consist largely of iron oxide.



A hearth made up in this manner will stand up satisfactorily, even at high temperatures, while the melt is rich in oxides, but will not satisfactorily resist the reducing conditions encountered in refining the steel to the highest degree of purity.

The basic electric process permits the super-refinement of the steel through the formation of a slag rich in calcium carbide and the elimination of air from the furnace. The degree of refinement is such that metallic oxides, such as iron and manganese oxides, can be completely reduced from the slag and driven into the metal. Such a reducing condition of the slag automatically cleans the metal of all oxides, in which condition its affinity for oxygen is greatly increased.

It has been found that, when the refining operation has reached a stage where the slag has been cleared of all except about 1 per cent. of iron and manganese oxides, a balance has been reached beyond which refinement cannot proceed without destruction of the furnace hearth. When attempts are made to obtain super-refinement of the metal and complete reduction of metallic oxides from the slag, the highly deoxidized metal reacts with the iron-oxide bond in the refractory reducing it to metallic iron. This reduction releases the bond on the surface of the refractory and permits the magnesite or dolomite mixture to float through the bath into the slag. The iron oxide still remaining in the released refractory not only contaminates the refined metal but deranges the slag and interferes with further refinement, often necessitating the removal of the slag and the formation of a new slag that is free from magnesia.

This condition not only defeats all attempts to get perfect refinement of electric steel but greatly increases cost, as the time consumed in overcoming the derangement of balance as the result of poor hearth material requires a tremendous expenditure of electrical energy. Cases have been observed where a 6-ton heat has required as much as 2000 kw.-hr. over the normal power load to overcome derangement of slag and metal caused by faulty hearth material.

The production of electric steel has been perfected to a remarkable degree but any further marked progress with the object of producing a perfectly refined product entirely free from oxides is prevented by the lack of proper material for the hearth, which will have a neutral reaction toward fully reduced slag and steel. This problem is of sufficient importance to the industry to warrant the most exhaustive study by ceramic engineers.

It is believed that a satisfactory refractory for basic electric furnace should have as a base magnesite or dolomite with a bonding material entirely free from iron oxide or other metallic oxides which can be reduced by oxygen-free metal or by the calcium-carbide slag. For this purpose, such materials as silica, alumina, magnesium salts, silicates of the alkaline earths, etc., might be found applicable.

## Effect of Zirconium on Hot-rolling Properties of High-sulfur Steels and the Occurrence of Zirconium Sulfide

ALEXANDER L. FEILD,\* M. S., NEW YORK, N. Y.

(New York Meeting, February, 1924)

IN A previous paper,<sup>1</sup> the experimental methods used and some of the results obtained in an extensive investigation of steels containing zirconium were described. The present paper considers in greater detail one of the most interesting of these effects, namely, the elimination of "red shortness" and the occurrence in steel of a compound of zirconium and sulfur.

A consideration of the actual percentages of zirconium, manganese, and sulfur in numerous steels in the light of behavior during rolling has led to new conclusions of the most practical import regarding the reciprocal relationships of these elements. The microscopic examination of high-sulfur steels containing zirconium has also been productive of interesting results. Before discussing the experimental data in question, it may be stated, briefly, that the reaction between zirconium and sulfur in molten steel may be represented by the simple equation,  $\text{Zr} + 2\text{S} = \text{ZrS}_2$ , and that the zirconium sulfide thus formed occurs in the finished steel in the form of gray-colored inclusions, closely resembling manganese sulfide and, like the latter, exhibiting plasticity at rolling temperatures. Molten steel containing zirconium retains such a negligibly small amount of oxygen in solution that the foregoing reaction goes to completion.

### HOT-ROLLING PROPERTIES OF HIGH-SULFUR STEELS WITH AND WITHOUT ZIRCONIUM

The chemical composition of twenty-eight steel ingots embracing eleven heats made in a basic-lined electric furnace is shown in Table 1. The practice followed in the manufacture of these high-sulfur steels was described in the previous paper. Table 1 also gives the behavior of the

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<sup>1</sup> Some Effects of Zirconium in Steel. *Trans.* (1923) 69, 848.

ingots during rolling and the condition of the rolled plate. Rolling practice for six of the eleven heats was given in Table 2 of the previous

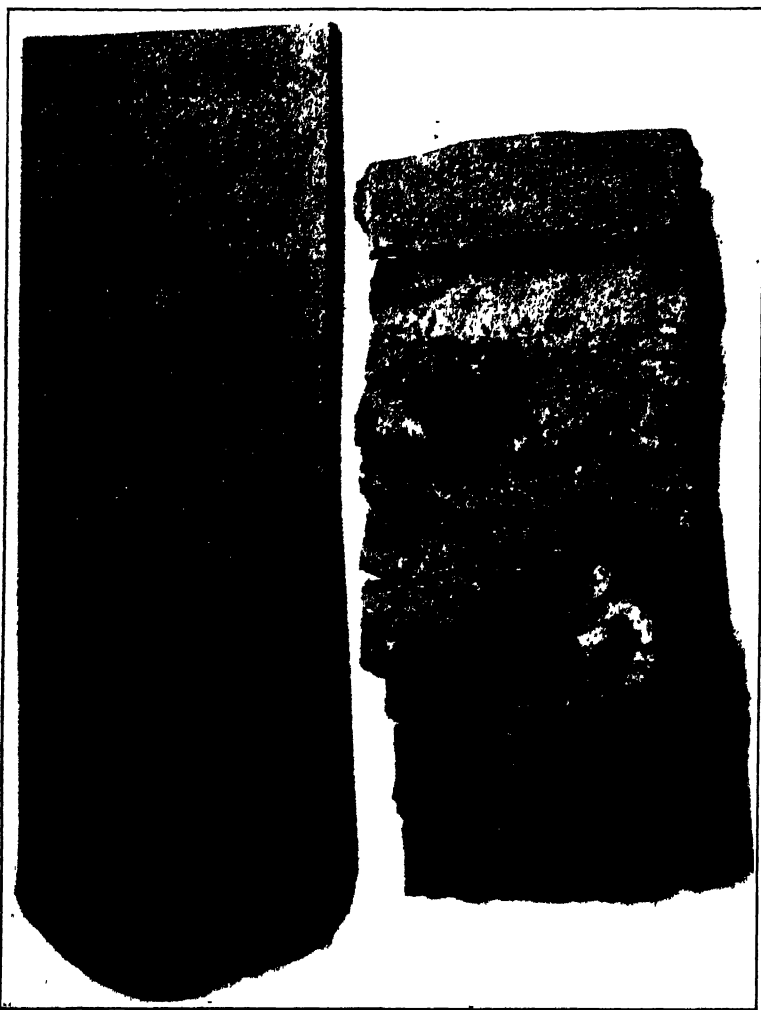


FIG. 1.—UPPER PART OF FINISHED PLATE FROM ZIRCONIUM-TREATED INGOT 305A AND UNTREATED INGOT 305B, WHICH BROKE TO PIECES IN ROLLS. THESE STEELS CONTAIN APPROXIMATELY 0.2 PER CENT. SULFUR AND 0.2 PER CENT. MANGANESE.

paper. The remaining five heats were rolled in the same mill under similar conditions of practice.

Five of the eleven ingots that contained no zirconium broke to pieces on the first or second pass through the rolls and all the rest, except 280B, showed "red shortness" in varying degrees, ranging from a roughening

of the edges of the plate to deep tearing that verged on complete breakage. Of the seventeen ingots containing zirconium, fourteen were satisfactorily rolled to plate and the remaining three were "red short" to a more or less

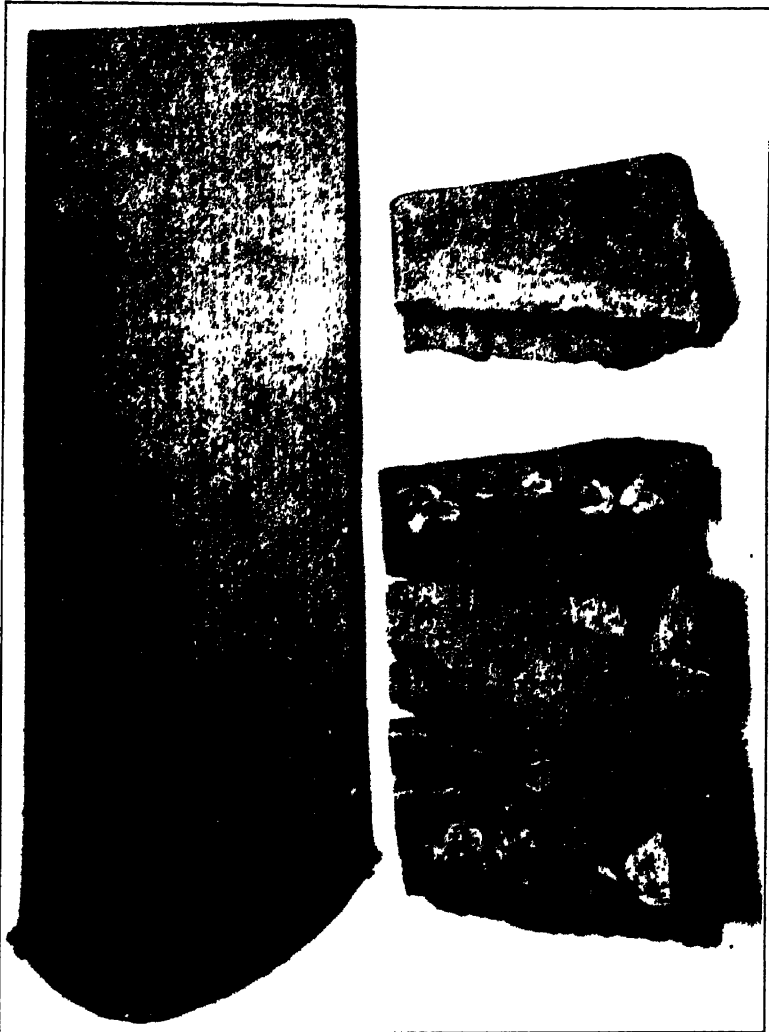


FIG. 2.—UPPER PART OF FINISHED PLATE FROM ZIRCONIUM-TREATED INGOT 306C AND UNTREATED INGOT 306B, WHICH BROKE TO PIECES IN ROLLS. THESE STEELS CONTAIN APPROXIMATELY 0.2 PER CENT. SULFUR AND 0.1 PER CENT. MANGANESE.

pronounced degree. None of the last-mentioned, however, broke to pieces during rolling.

Fig. 1 shows the upper part of the finished  $\frac{1}{2}$ -in. plate from the zirconium-treated ingot 305A and, beside it, the untreated ingot (305B)

from the same heat that broke to pieces in the rolls. Fig. 2 shows the finished plate from ingot 306C containing zirconium and of the corresponding ingot 306B that contained no zirconium and broke up on the first pass. These steels contained approximately 0.2 per cent. sulfur (see Table 1).

#### MINIMUM AMOUNTS OF MANGANESE AND OF ZIRCONIUM NECESSARY TO PREVENT RED SHORTNESS

It has been established by Arnold and Waterhouse<sup>2</sup> that when, because of a deficiency of manganese, iron sulfide occurs in steel, it exists as a separate constituent of pale brown color and not in solid solution in manganese sulfide. For this reason, it is permissible to assume that one part, by weight, of manganese in a steel will not have converted at best more than 0.584 part of sulfur to the relatively harmless form of dove-colored inclusions. This proportion is that represented by the theoretical composition of the sulfide, MnS. Similarly, it may be reasoned that one part of zirconium may not be reasonably expected to convert to zirconium sulfide more than 0.708 part of sulfur. This proportion is that existing in the compound ZrS<sub>2</sub>.

In 1876, it was stated by Hackney<sup>3</sup> that, to be forgeable, steels must contain from three to five times as much manganese as sulfur. In steel manufacture today, it is a generally accepted principle that some such large excess of manganese is necessary, the tendency being to place the ratio somewhere between four and eight.

McCance<sup>4</sup> has offered strong evidence in support of the view that the reaction  $\text{FeO} + \text{Mn} = \text{Fe} + \text{MnO}$  in steel is a balanced one and that a large excess of manganese is required for the reaction to go to practical completion toward the right. This inability of manganese, alone and in reasonable amount, to deoxidize steel completely is held to be responsible for the usual inefficiency with which it takes care of the sulfur content.

The ratios, by weight, of manganese to sulfur for the eleven steels of Table 1 that contained no zirconium are given in Table 2. The values range from 0.44 to 3.60. In examining these ratios and noting in Table 1 the condition of the corresponding steels, it will be observed that a complete break up in the rolls occurred only when the ratio fell below the theoretical value, 1.71, for the formation of MnS. However, the four steels with higher ratios than this, ranging from 1.78 to 3.60, showed indications of more or less pronounced red shortness. Ingot 280B, it is true, showed this property to an important degree only in

<sup>2</sup> *Jnl. Iron and Steel Inst.* (1903) **63**, 136.

<sup>3</sup> *Jnl. Iron and Steel Inst.* (1876) 63.

<sup>4</sup> *Jnl. Iron and Steel Inst.* (1918) **97**, 239.

the upper third of the plate; if this ingot had been cropped before rolling, to remove the pipe, a satisfactory plate would no doubt have been obtained. In the practice followed in the present investigation, the minimum manganese content necessary to prevent red shortness was less than 3.60 but definitely more than 2.23 times the sulfur content.

Unger<sup>6</sup> has demonstrated, in operations conducted on 6300-lb. ingots, the good hot-working properties of a series of high-sulfur, basic, open-hearth steels, and has found it possible to roll without difficulty a steel having a ratio of manganese to sulfur as low as 2.39. He was not able to roll satisfactorily two steels in which this ratio was 1.72 and 1.70, respectively.

The minimum ratio of manganese to sulfur in basic steels of the hypoeutectoid type may be tentatively placed at 2.3. In other words, in its reaction and combination with sulfur, manganese is not more than 74 per cent. efficient. Whenever, in plant practice, a ratio higher than 2.3 is needed to secure satisfactory hot-rolling properties, it is certain that manganese is being forced to carry out its sulfur-combining function in an environment less favorable than the optimum.

The ratios, by weight, of manganese to sulfur for the seventeen steels of Table 1 that contained zirconium are given in Table 3; the values range from 0.44 to 3.77. Examining these ratios, as before, and considering them in the light of the remarks on the condition of the rolled plate, reveal that many of the steels were entirely free from red shortness with far less than the theoretical ratio (1.71) of manganese to sulfur. For instance, ingot 333A, with a ratio of only 0.45, yielded a plate free from flaws. In the case of this steel, as well as a number of others, it is evident that zirconium has been responsible for converting into a form, harmless at rolling temperatures, by far the greater part of the total sulfur.

It is of interest to calculate what percentages of sulfur the zirconium and manganese contents of the steels of Table 3 are capable theoretically of holding in combination— as zirconium sulfide,  $ZrS_2$ , in the former case and as manganese sulfide,  $MnS$ , in the latter. These computed values are shown in Table 4, together with the sulfur percentages of the same steels, as shown by analysis. Column V of Table 4 contains the calculated ratios of total sulfur-combining power of zirconium plus manganese, in per cent. sulfur, to the per cent. sulfur actually present. When, for instance, this ratio is 1.41, as in the case of ingot 306A, this steel has sufficient zirconium plus manganese to take care theoretically of 41 per cent. more sulfur than is present. When the ratio is unity, the sulfur present is in proper amount exactly to account for the zirconium and manganese as their respective sulfides. In those cases where the ratio is less than unity, there must be iron sulfide in the steel.

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<sup>6</sup> *Iron Age* (1916) 97, 146.

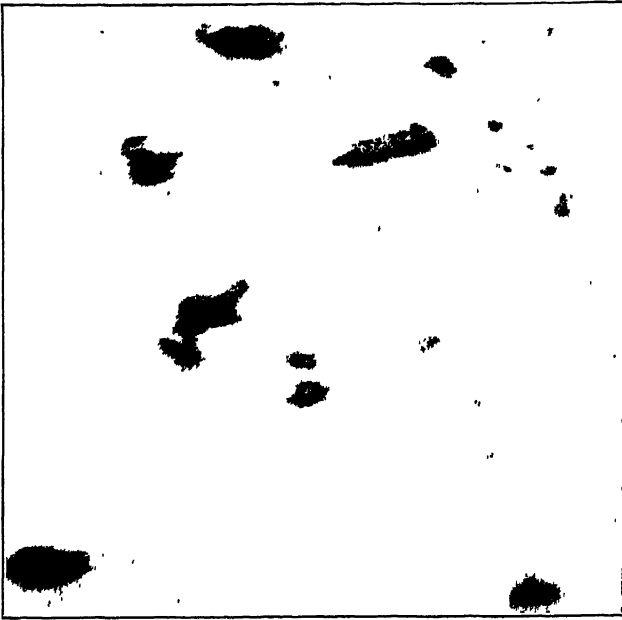


FIG. 5.—POLISHED, UNETCHED SECTION IN PLANE OF ROLLING SHOWING SULFIDE INCLUSIONS IN STEEL 332A.  $\times 500$ .

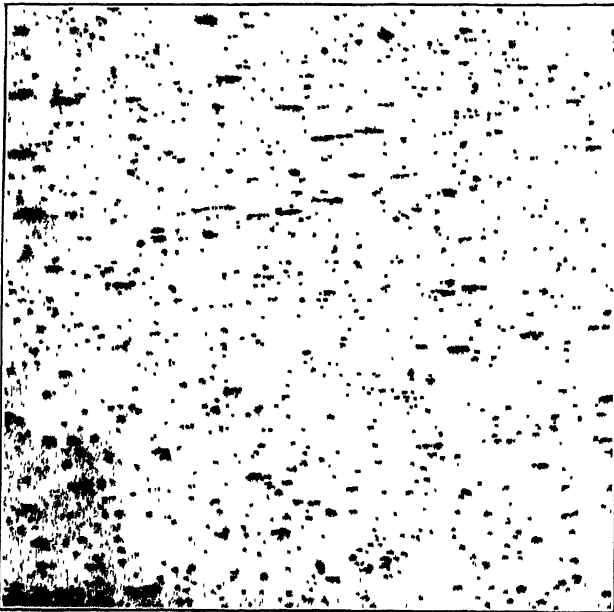


FIG. 6.—POLISHED, UNETCHED LONGITUDINAL SECTION, PERPENDICULAR TO PLANE OF ROLLING, SHOWING SULFIDE INCLUSIONS IN STEEL 332A, WHICH CONTAINS 0.311 PER CENT. SULFUR, 0.16 PER CENT. MANGANESE, AND 0.32 PER CENT. ZIRCONIUM.  $\times 100$ .

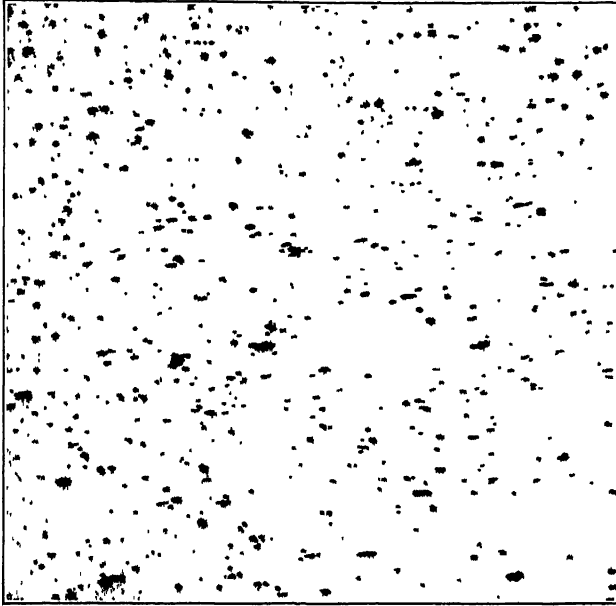


FIG. 7.—POLISHED, UNETCHED, TRANSVERSE SECTION, PERPENDICULAR TO PLANE OF ROLLING OF STEEL 332A.  $\times 100$ .

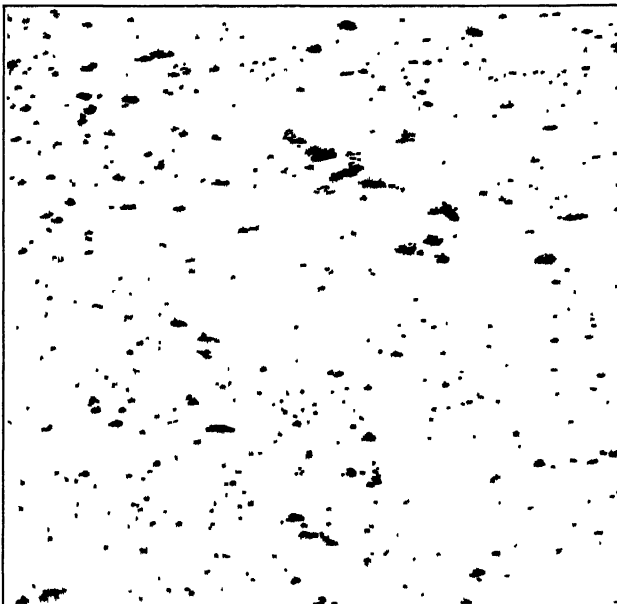


FIG. 8.—POLISHED, UNETCHED SECTION IN PLANE OF ROLLING OF STEEL 332A.  $\times 100$ .  
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by the combined action of the zirconium and manganese contents. Of the sulfur so combined, not more than 0.093 per cent. can be allotted to manganese, leaving at least 0.218 per cent. for formation of zirconium sulfide. On microscopic examination of this steel, only one predominating and significant type of inclusion is to be observed. The inclusions of this type are gray in color and show elongation in the direction of rolling. Their abundance and the low manganese content of the steels make it certain that only a small part of their total number can be manganese sulfide.

In order to expose to view the general shape of these inclusions, photomicrographs were taken of three sections corresponding to three planes at right angles, one plane being the plane of rolling, a procedure first used by Arnold.<sup>6</sup> A set of these at 500 diameters is shown in Figs. 3, 4 and 5, the specimens being taken from the rolled plate of ingot 332A. Figs. 6, 7 and 8 show the same sections at 100 diameters, the number and distribution of inclusions being shown to better advantage here than their shape, although the latter is apparent on close examination.

These photomicrographs were taken by the method of conical illumination devised by H. S. George.<sup>7</sup> This method gives depth and relief to the object photographed and brings out many structural features ordinarily obliterated or masked under vertical light. Among other things, it distinguishes definitely between depressions and elevations. The sulfide areas in the photomicrographs are depressed below the level of the surrounding metal.

#### IDENTITY OF ZIRCONIUM-SULFUR COMPOUND NOT DECOMPOSED BY 1:1 HYDROCHLORIC ACID

In the previous paper, analyses were presented to show that a portion of the sulfur content of zirconium-treated steels was not evolved as hydrogen sulfide in the course of the usual analysis by the evolution method, provided the amount of zirconium added to the molten steel exceeded 0.15 per cent. This critical value of 0.15 per cent. was considered as applicable to the particular kind of practice used in the manufacture of the steels in question and represented the percentage of zirconium consumed in reactions with dissolved oxygen and nitrogen. It was established that, over a wide range of steel compositions and amounts of added zirconium, the following relation held good to a surprisingly close approximation:

$$\text{Per cent. sulfur "fixed"} = \frac{\text{Per cent. added zirconium} - 0.15}{10}$$

where the percentage of sulfur fixed equaled that percentage of sulfur which failed to evolve hydrogen sulfide on acid treatment. In other

<sup>6</sup> *Metallographist* (1902) 5, 228.

<sup>7</sup> *Trans. Am. Soc. for Steel Treating* (1923).

words, for every part of zirconium added over and above 0.15 per cent., 0.10 part of sulfur is fixed in acid-insoluble form. The analytical data given as proof of this quantitative relation covered a range of sulfur percentages up to approximately 0.1 per cent. Plain carbon steels only were considered.

It is now known that the relation expressed in this equation holds equally well for alloy steels of a wide diversity of type. However, difficulty is encountered in extending the range of reliable application of the equation to more than 0.1 per cent. sulfur, whether for plain carbon or alloy steels. This difficulty is imposed by the limitations of the evolution method of analysis, at least in its present state of development.

For a number of reasons, it is not believed that the decline in amount of acid-evolved sulfur begins until zirconium is present in sufficient amount to have converted all sulfur to  $ZrS_2$ . This new conception makes the value of per cent. zirconium at which formation of the acid-insoluble compound starts a function of the sulfur content of the steel instead of a constant, 0.15, as given above. This is equivalent to stating that decrease in acid-evolved sulfur proceeds quantitatively on the completion of the reactions of zirconium with oxygen and nitrogen and on conversion of sulfur to  $ZrS_2$ .

$$\text{Per cent. sulfur fixed} = \frac{\text{Per cent. added zirconium} - (0.15 + 1.41S)}{10},$$

where  $S$  is the sulfur content of the steel in per cent. This revised equation expresses the observed facts to a closer approximation than did the original, particularly in the range above 0.05 per cent. sulfur where the value of the correction term,  $1.41S$ , becomes appreciable. This unusual quantitative relation has been confirmed by a number of gravimetric analyses made on the insoluble residues that remain after treatment with 1:1 hydrochloric acid.

It is not now believed that there is any simple combination of zirconium and sulfur in the relative proportions of 10 to 1, as might be inferred from the equation. Formation of acid-insoluble sulfur proceeds in the above orderly manner only when the sulfur content of the steel has been converted to the normal disulfide,  $ZrS_2$ , and is possibly brought about by a partition of excess zirconium between the steel and the pre-formed  $ZrS_2$ . If this is the case, the amount of sulfur fixed in a form not evolved by hydrochloric acid is a measure of the extent of formation of a zirconium-zirconium sulfide solid solution. As zirconium displays in all of its definitely known compounds a valence of four, it is not permissible to postulate the occurrence of a lower sulfide.

It is especially to be emphasized that fixed sulfur, in the sense of sulfur not evolved as hydrogen sulfide on treatment with 1:1 hydrochloric acid, has now acquired a meaning entirely different from that of the sulfur combined in the steel as the normal zirconium disulfide,  $ZrS_2$ .

## INCLUSIONS OF A HIGHLY EMULSIFIED TYPE

In all of the high-sulfur steels of Table 1 that contained no zirconium a highly emulsified type of non-metallic inclusion occurred, visible only at high magnifications in the ferrite areas of etched sections. This fine emulsion was absent from the steels containing zirconium. Fig. 9 shows the occurrence of the emulsion in steel 368B, which contained 0.132 per cent. sulfur. Fig. 10 is the corresponding photomicrograph of steel 368C, which contained 0.133 per cent. sulfur, and 0.20 per cent. zirconium. The cubic crystal in the latter section is an inclusion of zirconium nitride. The magnification in both cases is 1000 diameters.



FIG. 9.—POLISHED SECTION, ETCHED WITH 5-PER CENT. ALCOHOLIC PICRIC ACID AND SHOWING FINELY DIVIDED INCLUSIONS IN FERRITE AREAS OF STEEL 368B, WHICH CONTAINED NO ZIRCONIUM.  $\times 1000$ .

The chemical composition of this emulsion is not positively known; however, as pointed out in the previous paper it probably consists of very finely divided particles of oxide or sulfide of iron.

## SULFIDE INCLUSIONS AND MECHANICAL PROPERTIES

In Tables 18 and 19 of the former paper, the longitudinal and transverse mechanical properties were reported for five of the eleven high-sulfur heats now under consideration. Additional data for heats 367 and 368 are given here in Tables 5 and 6. Tests were conducted on the plate in the as-rolled condition.

Differences between corresponding test values obtained on specimens taken longitudinally and transversely are quite generally ascribed to the presence of non-metallic inclusions elongated in the direction of rolling. To find, therefore, that steels containing three to ten times as much sulfur as is permissible under the usual specifications show ratios of longitudinal to transverse properties of the same order of magnitude as are frequently encountered in commercial steels is rather surprising. The existence of directional properties or mechanical anisotropy in rolled products is probably due to more than one factor.



FIG. 10.—SAME AS PRECEDING, FOR STEEL 368C WHICH CONTAINED ZIRCONIUM.  
× 1000.

#### SOURCE OF ZIRCONIUM

Zirconium has been introduced into the steels described both here and in the former paper as an alloy of zirconium, silicon, and iron. This alloy is commonly referred to as silicon-zirconium. The chemical composition of the alloy was reported in a number of analyses in the former paper (Table 1).

#### SUMMARY

The hot-rolling properties of a number of high-sulfur ingots, with and without a zirconium content, have been described, as well as the appearance and condition of the plate rolled therefrom. The sulfur content of the steels ranged from 0.075 to 0.320 per cent. It is shown that:

1. Zirconium eliminates red shortness when present in the finished steel in the proportion of 1.41 parts or more of zirconium to 1 part of sulfur; the ratio 1.41 corresponds to the formation of the normal zirconium sulfide,  $\text{ZrS}_2$ .

2. Zirconium sulfide, like manganese sulfide, is plastic at rolling temperatures and, in polished sections, is visible as ovoid or elongated gray inclusions.

3. Evidence is offered in support of the view that oxygen is jointly responsible with sulfur for red shortness in steels that contain manganese only as a sulfur-combining element.

4. Zirconium, unlike manganese, is not required in the finished steel in amount greater than that theoretically required for formation of zirconium sulfide, because of its powerful deoxidizing action.

5. In amount greater than that required to form the sulfide, zirconium confers on the sulfur content of the steel the property of insolubility in 1:1 hydrochloric acid, the percentage of sulfur thus rendered insoluble being proportional to the excess of zirconium in the ratio of 1 part of sulfur to 10 of zirconium. An explanation of this phenomenon is offered.

#### ACKNOWLEDGMENTS

The author wishes to acknowledge the kind assistance of J. H. Critchett, who has read the manuscript of this paper and offered valuable suggestions toward its preparation, and of H. S. George, whose coöperation and aid with the microscope has been of material help. The preparation of metallographic specimens and of the illustrations that accompany the text has been the work of J. R. Vilella and W. P. Melville, respectively.

TABLE 1.—*Analyses and Hot-rolling Properties of High-sulfur Steels, with and without Zirconium*

Heat Number	Ingot	Per Cent Added Zirconium	Per Cent. Carbon	Per Cent Silicon	Per Cent Manganese	Per Cent Phosphorus	Per Cent Sulfur*	Per Cent. Zirconium,	Condition of Plates
280	A	0.15	0.46	0.15	0.28	0.017	0.077	0.13	Satisfactory, no imperfections
	B	none	0.42	0.14	0.27	0.019	0.075		Satisfactory,† roughened along upper edges.
285	A	0.16	0.98	0.15	0.37	0.018	0.116	0.15	Satisfactory, no imperfections.
	B	none	0.99	0.21	0.38	0.018	0.110		Badly seamed along edges
286	A	0.42	0.40	0.44	0.26	0.025	0.109	0.33	Satisfactory, no imperfections.
	B	none	0.37	0.44	0.25	0.025	0.112		Crack in base; badly roughened along one edge
287	A	0.42	0.59	0.41	0.20	0.016	0.082	0.34	Satisfactory, no imperfections
	B	none	0.57	0.45	0.19	0.016	0.107		Crack in base, seams along edges.
305	A	0.47	0.39	0.40	0.13	0.019	0.190	0.25	Satisfactory; no imperfections
	B	none	0.32	0.20	0.17	0.015	0.224		Ingot broke up on first pass
	C	0.22	0.37	0.23	0.12	0.017	0.210	0.19	Torn at intervals along both edges
306	A	0.40	0.29	0.43	0.14	0.025	0.182	0.25	Satisfactory, slight roughness on upper part of one edge.
	B	none	0.27	0.27	0.13	0.024	0.189		Ingot broke up on second pass
	C	0.23	0.27	0.24	0.14	0.024	0.186	0.18	Satisfactory; no imperfections
318	A	0.24	0.36	0.27	0.32	0.021	0.187	0.16	Satisfactory, no imperfections
	B	none	0.36	0.25	0.33	0.021	0.190		Badly torn along both edges.
332	A	0.47	0.35	0.44	0.16	0.014	0.311	0.33	Satisfactory, ragged spot near top on one edge
	B	none	0.37		0.14		0.320		Ingot broke up on first pass.
	C	0.25	0.34	0.22	0.14	0.013	0.319	0.18	Badly torn along edges
333	A	0.43	0.33	0.38	0.14	0.013	0.310	0.29	Satisfactory, no imperfections.
	B	none	0.36		0.15	0.014	0.298		Ingot broke up on first pass.
	C	0.22	0.32	0.20	0.15	0.016	0.311	0.19	Torn at one point along edge; edges badly roughened.
367	A	0.40	0.66	0.46	0.19	0.055	0.310	0.20	Satisfactory; no imperfections
	B	none	0.66	0.28	0.22	0.044	0.303		Ingot broke up on second pass
	C	0.23	0.66	0.26	0.17	0.059	0.318	0.16	Satisfactory, a few seams along edge near top.
368	A	0.40	0.15	0.28	0.16	0.010	0.132	0.30	Satisfactory; no imperfections.
	B	none	0.15	0.27	0.15	0.010	0.132		Very badly torn and disintegrated.
	C	0.27	0.14	0.25	0.14	0.011	0.133	0.20	Satisfactory; a few folds on edge near top.

\* Sulfur determined by gravimetric method.

† The ingots were not cropped before rolling; imperfections near top of plate, corresponding to "piped" portion of ingot not regarded as significant.

TABLE 2.—*Influence of Relative Percentages of Manganese and Sulfur on Hot-rolling Properties of Steels without a Zirconium Content*

Heat Number	Ingot	Ratio of Per Cent. Mn to Per Cent. S	Hot-rolling Properties
280	B	3.60	Satisfactory
285	B	3.45	Bad
286	B	2.23	Poor
287	B	1.78	Poor
318	B	1.60	Bad
368	B	1.14	Bad
305	B	0.76	Broke up
367	B	0.72	Broke up
306	B	0.69	Broke up
333	B	0.50	Broke up
332	B	0.44	Broke up

TABLE 3.—*Influence of Relative Percentages of Manganese and Sulfur on Hot-rolling Properties of Steels Containing Zirconium*

Heat Number	Ingot	Ratio of Per Cent. Mn to Per Cent. S	Hot-rolling Properties
280	A	3.77	Satisfactory
285	A	3.28	Satisfactory
287	A	2.41	Satisfactory
286	A	2.38	Satisfactory
318	A	1.71	Satisfactory
368	A	1.21	Satisfactory
368	C	1.05	Satisfactory
306	C	0.77	Satisfactory
306	A	0.75	Satisfactory
305	A	0.68	Satisfactory
367	A	0.61	Satisfactory
305	C	0.57	Bad
367	C	0.53	Satisfactory
332	A	0.51	Satisfactory
333	C	0.48	Bad
333	A	0.45	Satisfactory
332	C	0.44	Bad

TABLE 4.—*Influence on Hot-rolling Properties of Relation between Maximum Theoretical Sulfur-combining Capacity of Zirconium Plus Manganese and Actual Percentage of Sulfur in Steels Containing Zirconium*

Heat Number	Ingot	I. Per Cent. Sulfur by Analysis	II Sulfur Equivalent (Per Cent. S) of $\text{Mn}(0.584 \times \text{Mn})$	III. Sulfur Equivalent (Per Cent. S) of $\text{Zr}(0.708 \times \text{Zr})$	IV. Total- S Equiva- lent	V Ratio of Column IV to Column I	Hot-rolling Properties
287	A	0.082	0.116	0.241	0.357	4.35	Satisfactory
286	A	0.109	0.151	0.234	0.385	3.53	Satisfactory
280	A	0.077	0.163	0.092	0.255	3.44	Satisfactory
285	A	0.116	0.215	0.106	0.157	2.77	Satisfactory
368	A	0.132	0.093	0.212	0.305	2.31	Satisfactory
368	C	0.133	0.081	0.142	0.223	1.66	Satisfactory
318	A	0.187	0.186	0.113	0.299	1.60	Satisfactory
306	A	0.182	0.081	0.176	0.257	1.41	Satisfactory
305	A	0.190	0.076	0.176	0.252	1.32	Satisfactory
306	C	0.186	0.081	0.127	0.208	1.12	Satisfactory
332	A	0.311	0.093	0.234	0.327	1.05	Satisfactory
367	A	0.310	0.110	0.205	0.315	1.02	Satisfactory
305	C	0.210	0.070	0.135	0.204	0.97	Bad
333	A	0.310	0.081	0.205	0.286	0.92	Satisfactory
333	C	0.311	0.087	0.135	0.212	0.70	Bad
367	C	0.313	0.099	0.113	0.212	0.67	Satisfactory
332	C	0.310	0.081	0.127	0.208	0.65	Bad

TABLE 5.—*Mechanical Tests on High-sulfur Rolled Plate (Longitudinal)*

Heat Number	Per Cent. Added Zirconium	Yield Point, Lb. Per Sq. In.	Ultimate Strength, Lb. Per Sq. In.	Elonga- tion in 2 In., Per Cent.	Reduction of Area, Per Cent.	Isod Number Ft.-Lb.	Brinell
367A	0.40	45,424	114,009	12.5	24.4	7.8	202
C	0.23	46,605	107,993	13.8	24.2	7.2	204
368A	0.40	32,963	59,008	29.0	63.6	62.4 <sup>a</sup>	95
C	0.27	29,438	54,124	30.5	58.1	58.7 <sup>a</sup>	86

<sup>a</sup> Test piece bent, not entirely broken.

The B ingots of both heats, containing no zirconium, broke up during rolling.

TABLE 6.—*Ratios of Longitudinal to Transverse Properties*

Heat Number	Per Cent. Added Zirconium	Elongation in 2 In., Per Cent.	Reduction of Area Per Cent.	Isod Number, Ft.-Lb.
367A	0.40	1.60	2.49	1.43
C	0.23	2.12	3.32	1.41
368A	0.40	1.14	1.30	1.41
C	0.27	0.97	1.22	1.22



## DISCUSSION

BERAM D. SAKLATWALLA,\* Bridgeville, Pa.—The author has taken the standpoint from a chemical basis of combination of sulfur and zirconium, but one very important point has been overlooked. The complete data for drawing another sort of a conclusion are present in the paper but this conclusion has not been drawn.

The author speaks of some part that oxygen plays in combinations of manganese sulfide and zirconium sulfide. He also mentions that steels containing non-metallics and oxides show emulsification phenomena, and that the bad properties of such steels might be due to the presence of such emulsions. It may be that the strongly deoxidizing power of zirconium puts the iron content, or the body of the steel, in such physical shape as to allow the non-metallics to diffuse through it, or rather to coagulate into harmless globules, or what he terms plastic sulfides. So, really, the effect of making sulfur harmless by zirconium might be purely of a secondary nature.

The question then would be as to why other deoxidizers do not accomplish the same thing. We know that manganese does the same thing, but to a lesser extent. The paper shows that we require a much larger amount of manganese to complete this reaction than would be necessary theoretically. That might be due to the less strongly deoxidizing power of manganese as compared with zirconium. Zirconium is perhaps the most powerful deoxidizing element that we know of that can be used in steel, and this good effect might be purely due to the cleansing effect of removing the oxygen and putting the other non-metallics into a more coagulable form.

BRADLEY STOUGHTON,† Bethlehem, Pa.—Will this sulfur that is combined with the zirconium come out on a sulfur print? Can the insolubility of the zirconium sulfide be used in any way for removing the sulfur, as is done in the case of manganese, although so slowly?

ALEXANDER L. FEILD.—The question of the degree of insolubility of zirconium sulfide in steel at temperatures above the liquidus for the iron-carbon system cannot be answered definitely. That zirconium sulfide may become, in part, insoluble before freezing of the metal occurs has been amply demonstrated by the substantial elimination of sulfur in the ladle under favorable conditions. It is not, however, believed that the use of zirconium for actual elimination of sulfur from steel is practicable in most instances.

The effect of zirconium sulfide on a sulfur print depends on whether an excess of zirconium over and above that required for the formation of

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the normal sulfide has been used or not. The normal sulfide ( $ZrS_2$ ) is attacked by dilute sulfuric acid, although not as rapidly as is manganese sulfide, and its presence is therefore disclosed. By the employment of an excess of zirconium, as above defined, the solubility of zirconium sulfide may be progressively decreased until a point is reached at which no trace of sulfur appears in the sulfur print.

I do not recall having seen any data that prove that manganese eliminates sulfur from steel in the ladle, due to separation of manganese sulfide. This separation would appear to occur appreciably only in the case of a pig-iron mixer or in a ladle of cast iron, in both of which instances the metal has a considerably lower melting point.

ANDREW M'CANCE, Motherwell, Scotland (written discussion).—Of the elements that had the power of precipitating sulfur from its solution in molten iron, manganese was by far the most important; aluminum was also effective, though less known; now this paper has added zirconium to the number. The beneficial action of such elements is, as the author has pointed out, closely connected also with their behavior toward oxide compounds, which subject offers a wide field for research. It is possible, for instance, in bath samples, taken from basic open-hearth charges, to obtain two tests at different stages in the course of the heat, in which the contents of sulfur and manganese are practically identical, and yet their behavior during forging will be quite different—one showing marked red shortness and the other an entire absence of this condition. It is obvious, in such a case, that sulfur, in itself, is not the cause of the red shortness, while other work has shown equally that excess oxides in pure steel did not lead to red shortness above  $900^{\circ}C$ . It seemed to be their combined presence that was so detrimental.

Similarly, therefore, in determining the action of the agents that remove red shortness, it might be that, if the effect of zirconium was to remove oxides alone, the red shortness, due to sulfur, might equally disappear, although insufficient manganese was present to combine with the sulfur.

In this connection, it is hazardous to try to identify a microconstituent by visual examination alone, unless it has definite characteristics, and it would enhance the value of this if the author would explain, in detail, the reasons by which he was led to decide that the gray constituent was  $ZrS_2$ . In a long endeavor, the writer has never met with a single authentic case of even moderately pure manganese sulfide in commercial steels. Every example of dove-gray inclusion that he has been able to analyze has consisted of manganese silicate and oxide, with, at the most, 7 per cent. sulfur. The dove-gray inclusions in the author's steels might be solid solutions of  $MnS$ ,  $MnO$ ,  $ZrO$ , and  $ZrS_2$ , and be all of the one kind. It is just possible that the author's conclusions regarding the zirconium

compound concerned in the reactions might be modified if the exact composition of the inclusions were known. An additional reason for this suggestion is found in Fig. 9, as the emulsified inclusions shown in this photograph are very similar in appearance to the oxide specks found in low-carbon, basic, open-hearth steel, which are reducible by heating in hydrogen.

GEORGE F. COMSTOCK,\* Niagara Falls, N. Y. (written discussion).—This paper shows that zirconium is more effective than manganese in improving the rolling quality of steels abnormally high in sulfur. It would be instructive however if the author would compare the cost of preventing red shortness by zirconium with the cost of obtaining the same effect by manganese. The zirconium additions required for combining with all the sulfur seem rather large, considering the price of this metal. The failure of manganese to react favorably with all the sulfur in steel, unless a large excess is present above the theoretical amount, should not be blamed on its weakness as a deoxidizer, as implied in conclusion 4. The fact that manganese is a true alloying element in steel, reacting with carbon to form part of the pearlite, should be taken into consideration.

Some proof should be given for the statement that zirconium reacts with sulfur in steel according to the simple equation  $\text{Zr} + 2\text{S} = \text{ZrS}_2$ . The mere statement of this formula seems hardly conclusive. The metallographic evidence submitted would indicate that the sulfide formed is at least a mixture or compound of manganese and zirconium sulfides, and possibly containing iron sulfide also.

We should probably all be more careful to distinguish between the metallographic and chemical conceptions of the inclusions in steel. For instance, the metallographic constituent iron sulfide is rarely present in commercial steels, yet as the author stated in the discussion of his previous paper<sup>8</sup> a chemical compound of iron and sulfur undoubtedly exists in all steels as a part of the metallographic constituent known as manganese sulfide. Arnold and Waterhouse, in the reference quoted in the present paper to deny the existence of any iron in the sulfide constituent of normal steels, were correct only in the metallographic sense. Much more extensive investigations by Levy<sup>9</sup> and Röhl<sup>10</sup> and a statement by Law,<sup>11</sup> though ignored by the author, certainly show that the constituent commonly called "manganese sulfide" in steel really contains varying amounts of iron, also in combination with sulfur. The iron sulfide present in this form is as harmless as manganese sulfide and is usually

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<sup>8</sup> Some Effects of Zirconium in Steel. *Trans.* (1923) 69, 848.

<sup>9</sup> Carnegie Schol. *Mem.*, 3, 282.

<sup>10</sup> Carnegie Schol. *Mem.*, 4, 28.

<sup>11</sup> *Jnl. Iron and Steel Inst.* (1907), 2, 94.

ignored by metallographists, to whom the term "iron sulfide" means the distinctive brownish constituent described by Arnold and Waterhouse.

No evidence is submitted by the author to show that zirconium sulfide exists in steel in any purer state than manganese sulfide, so that it is most reasonable to assume that it merely enters into the sulfide mixture that steel generally contains. The working out of the correct quantitative relation between zirconium and sulfur in steel is thus undoubtedly hindered and complicated by the failure of zirconium sulfide to exist in the pure state. The assumption that oxygen must be responsible for red shortness in high-sulfur steel would not have been required if the unwarranted assumption that the sulfide inclusions in steel are chemically pure compounds had not first been made.

A. L. FIELD.—Mr. Comstock credits me with the statement that "a chemical compound of iron and sulfur undoubtedly exists in all steels as a part of the metallographic constituent known as manganese sulfide." I had no intention of leaving this impression by any statement which I made in the course of the discussion to which he refers. I would appreciate it very much if Mr. Comstock would say just where this statement occurs.

It seems to be Mr. Comstock's conviction that conclusive experimental proof has been obtained by other investigators (particularly Levy, Röhl and Law) that the normal dove-colored constituent in steel that is termed "manganese sulfide" contains varying and significant amounts of iron sulfide; and that I have failed to take this fact into account.

In my treatment of the subject I confined myself largely to the metallographic evidence and hot-working observations advanced by Arnold and Waterhouse because of the practical significance of their work and the scale on which their operations were conducted. Although I did not refer to the fact, I had made a careful study of the work of the other investigators to whom Mr. Comstock refers and had concluded that their findings did not necessarily disprove the conclusions of Arnold and Waterhouse.

Law,<sup>12</sup> for instance, in referring to the occurrence of iron sulfide says: "When it does occur it is usually found with, and often completely surrounding, the manganese sulfide." He later says that manganese sulfide varies very much in color and composition. Also (on page 97) "the lighter color is found in steels high in sulfur and low in manganese, and is probably due to the manganese sulfide dissolving a certain amount of iron sulfide." No chemical evidence whatever is advanced. Law's stand is probably summed up in the statement (on page 95): "The microscopical examination shows that in commercial steels no fewer than

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<sup>12</sup> *Loc. cit.*, 96.

five distinct impurities may be present; *viz.*, sulfide of iron, sulfide of manganese, silicate of iron, silicate of manganese, and oxide of iron (or possibly oxide of manganese). It must be understood that these do not occur in a pure state, but *their composition is essentially that of the compounds named.*" [The italics are mine.] Law is in substantial agreement with Arnold and Waterhouse. No one would attempt to maintain that normal manganese sulfide inclusions are chemically pure MnS. I have nowhere stated, however, that iron sulfide is a necessary or significant constituent of the normal dove-colored inclusions. If it were a significant constituent, steels with a lower ratio of manganese to sulfur than that which corresponds to the formation of MnS ought to be free from "red shortness," in some instances at least. Evidently, a process of solution of iron sulfide in manganese sulfide to form plastic inclusions should relieve manganese of a portion of its work. Although steels containing zirconium are to be considered an exception, practical experience in general has shown that steels containing more sulfur than that which can be accounted for as existing in combination with manganese as the normal sulfide are subject to "red shortness."

Levy<sup>13</sup> refers to only one apparently brief series of experiments with steel. He agrees with Law that the depth of color of the manganese sulfide inclusions depends on the composition of the steel; he makes the following statement (p. 307): "The darker varieties of the sulfide, corresponding to the greater freedom from iron, are more usually found in the steels of higher manganese and carbon proportions; whilst in steels containing small amounts of these constituents iron sulfide may be occasionally distinguished, not infrequently associated with manganese sulfide, as already described." Levy describes (p. 307) the two types of inclusions as "very pale yellow-brown areas resembling iron sulfide" and "exceedingly pale lavender-colored patches." His very able work on the system MnS-FeS, which is described in the same paper, does not bear directly on the point at issue, because of the absence of any uncombined iron in the melts. Iron sulfide, in the absence of iron, dissolves in manganese sulfide up to 50 per cent. by weight. It is not proved that a solid solution of the two sulfides separates from iron on solidification.

Röhl<sup>13</sup> confined himself to experiments with 30-gm. melts of steel. The conclusions drawn therefrom, as well as from the data which he had obtained on the system FeS-MnS, deserve no particular attention here. In so far as the system FeS-MnS is concerned, he fails to check the data of Levy. Conclusions based on these erroneous results are employed in his later deductions regarding occurrence of sulfides in the very small melts employed. Röhl himself admits the absence of conditions approaching those of regular practice.

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<sup>13</sup> *Loc. cit.*

Zirconium is known to form only one sulfide and the composition of this sulfide can be expressed by the formula  $\text{ZrS}_2$ . In conclusion, it may be stated that the reaction expressed by the simple equation  $\text{Zr} + 2\text{S} = \text{ZrS}_2$ , explains the elimination of "red shortness" by means of zirconium in a remarkably quantitative manner, as shown by the analytical data and hot-rolling observations recorded in the tables. These facts may not constitute a rigid proof in the academic sense. In this connection, however, I believe Mr. Comstock will agree with me that proof of this sort has been obtained in the case of none of the deoxidizers commonly employed in steelmaking although certain of these have been in general use over a long period of years.

## Effect of Coke Combustibility on Stock Descent in Blast Furnaces\*

By P. H. ROYSTER† AND T. L. JOSEPH,‡ MINNEAPOLIS, MINN.

(New York Meeting, February, 1924)

IN A study of the blast-furnace process, the Bureau of Mines has made many experiments for the purpose of determining the exact nature of the combustion of coke in the neighborhood of the tuyeres. Two papers<sup>1</sup> presented at a meeting of this Institute discussed somewhat the practical aspects of coke combustibility in its relation to the operation of the blast furnace. In a later paper,<sup>2</sup> Sherman and Kinney discussed the possible effect of variations in the combustibility of cokes on the furnace operation, and find that the "reoxidation theory" of Koppers and the "heat concentration theory" of Brassert<sup>3</sup> are insufficient to explain the variation in the conduct of different cokes that has been observed by furnace operators. In their report to the D-5 Committee of the American Society for Testing Materials, with which the Bureau of Mines has been coöperating, Perrott and Fieldner<sup>4</sup> seem to agree with Sherman and Kinney that, for practical purposes, the nature of the combustion of coke at the tuyeres of any furnace is constant and is affected neither by the physical properties of the coke nor by the nature of the furnace operation. They omit as unimportant any tests on the combustibility of coke from their proposed methods for standard tests on coke. In the last two papers, it is pointed out that performance tests, in which all other factors except coke quality are kept constant, are to be desired and

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<sup>1</sup> Perrott and Kinney: Combustion of Coke in the Blast-furnace Hearth. *Trans.* (1923) 69, 543.

Sherman and Blizard: Combustion of Blast-furnace Cokes in Fuel Beds. *Trans.* (1923) 69, 526.

<sup>2</sup> Sherman and Kinney: Combustibility of Blast-furnace Coke. *Iron Age* (June 28, 1923) 111, 1839.

<sup>3</sup> Modern American Blast Furnace Practice. *Year Book*, Amer. Iron and Steel Inst. (1914) 4, 15.

<sup>4</sup> Perrott and Fieldner: Properties of Metallurgical Coke. *A. S. T. M.* (June, 1923).

it is suggested that such a research can be conducted with the Bureau's experimental blast furnace at Minneapolis.

It is difficult to determine to what extent furnace operators and coke producers are convinced that the data collected by Perrott and Kinney prove that coke combustibility is not an important factor in blast-furnace operation. At first, it would seem, from the gas analyses taken across the tuyere zone of eleven furnaces, that the variations in the locations of the points of disappearance of oxygen and carbon dioxide are too small to produce any noticeable change in the operation of the furnace; these results cannot be readily reconciled with the differences observed by operators in the performance of coke in the blast furnace. It seems safe to conclude, however, that Perrott and Kinney have verified the discovery of Ebelman, in 1841, that all of the coke burned by the blast is consumed within 30 to 40 in. from the tuyeres. In their original report, Perrott and Kinney collect into one table the work of previous similar investigations. Of these early investigators, Van Vloten,<sup>5</sup> in 1893, conducted the most systematic investigation of coke combustion, although his data were taken from only one furnace. Van Vloten's gas samples were not confined, however, to points along the center line of the tuyeres; he covered the whole of the tuyere plane, also a plane above and another plane below the level of the tuyeres. The region of combustion was found to approximate spheres with centers corresponding to the center of the tuyeres. Although this conclusion would readily follow from the work of Perrott and Kinney, it might be suggested, because the coke in the face of the tuyeres breaks up the jet action, that the percentages of  $O_2$  and  $CO_2$  might be found to vary differently depending on the angle of approach to the tuyere. A number of furnace operators have expressed the opinion that the combustion zone extends farther above the tuyere plane than it does toward the center of the furnace along the axis of the tuyere. Work is now under way, in the Birmingham district, to obtain further information on this point by exploring a plane above the tuyere level.

It is the purpose of the present paper to discuss the suggestion of Van Vloten that as all the coke disappears in isolated regions located at the nose of the several tuyeres, it is necessary to assume that the descent of the coke in the bosh is not in vertical lines but that the flow is analogous to the motion of a liquid through a funnel, it being supposed that a funnel is mounted over each tuyere. This would leave a large part of the hearth and bosh filled with practically stationary coke; it is probable that stationary coke exists not only in the center of the hearth but also between the tuyeres. The effect of such a mass of coke lying at rest in the bottom of the hearth on the motion of the stock in the

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<sup>5</sup> *Stahl und Eisen* (1893) 13, 26-30.



furnace, as a whole, is impossible to predict, and Van Vloten suggested that its effect should be studied.

Acting on this suggestion of Van Vloten, the writers tried to study, in a simple way, the effect of coke combustibility on the movement of the charge in a blast furnace, by means of small model furnaces. The use of such models was suggested by Bell and a most excellent series of such experiments was published in the *Transactions* in 1888.<sup>6</sup> It is unfortunate that the data of Van Vloten were published five years after the experiments of Richards and Lodge, instead of five years before.

The model experiments of Richards and Lodge were carried out with a vertical model of wood and glass 40 in. high, the furnace lines of the model being those of Edgar Thompson Furnace D, of 1885. The model was filled by the bell-and-hopper device, the charge being various mixtures of sand and pebbles. These investigators discussed, in their paper, the obvious criticisms applicable to such a model and termed their experiments crude and defective but hoped that "they would throw some light on the difficult question of furnace feeding," which result they accomplished. The most serious fault with the manner of conducting the experiments was the method of removing the sand and pebbles from the bottom of the model. In most cases, the materials were removed uniformly across the hearth level; but in several cases from near the center of the hearth. It appears that little importance was attached to this phase of the experiments, the natural assumption seeming to be that combustion extended throughout the plane of the tuyeres. From the location of the zones of combustion, as determined by actual experiment, the materials representing the blast-furnace charge should have been removed from isolated regions near the edge of the hearth.

The writers have carried on experiments with model furnaces for several years. The purpose of most of these experiments was in no way connected with the question of furnace filling. In one phase of the writers' work, the problem of furnace lines has been predominant. Experience with these models has convinced them that such experiments are of great value in helping the mind to visualize the course of the solid charge in its path downward through the furnace. After trying a number of possibilities, the following device has been adopted. A smooth wooden board is inclined at an angle of about 10° to 20°. On this board the lines of the furnace to be examined are drawn to scale and pieces of cardboard are glued to the board to correspond to the furnace walls; the space within, corresponding to the furnace proper, is filled one layer thick with small lead shot, 0.16 in. diameter, which would correspond in the actual furnace to 5-in. spheres. A definite number of shot is removed from the tuyere zone at those places where the lumps of coke

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<sup>6</sup> Richards and Lodge: Descent of the Charge in an Iron Blast-furnace. *Trans.* (1888) 16, 149-162.

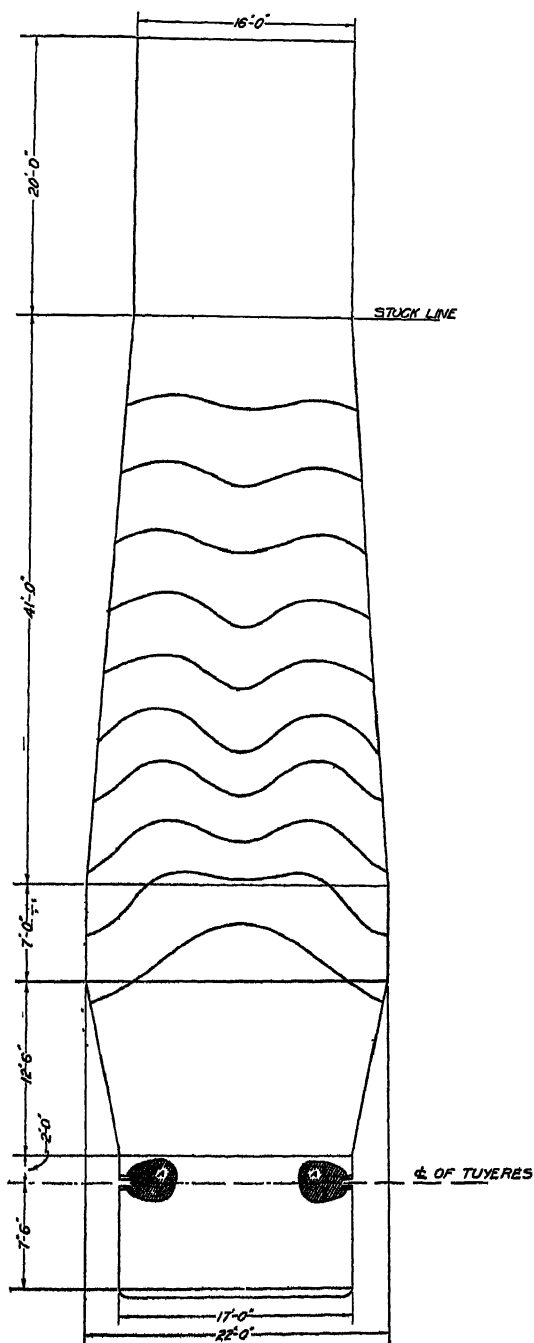


FIG. 1.—LINES OF REPRESENTATIVE AMERICAN FURNACE: ISOCHRONOUS LINES WITH NORMAL COMBUSTIBILITY.

are supposed to be burned by the blast, and the overlying mass slides down under the influence of gravity, new shot being charged to keep the stock line constant. A suitable number of the shot are etched with acid, plated with copper, or otherwise marked in order that they may be distinguished one from another. The path taken by the shot through the model furnace and the relative speeds with which the various shot travel are measured by noting the position of the marked shot from time to time.

For the present purpose, the design selected corresponded as nearly as possible to a representative modern American blast furnace; the lines are shown in Fig. 1, which is a composite drawing of the lines of fifty furnaces now or recently in blast. The curved lines indicate the shape and position of a row of shot after a fixed number have been removed from the neighborhood of the tuyeres quantitatively to correspond to the actual combustion of coke lumps calculated from the gas composition found in the experiments of Perrott and Kinney. These curves are the average of six tests and denote the position of shot that have been in the furnace the same length of time. Richards and Lodge have called them isochronous lines. In charging alternately groups of differently marked shot, the layers retain their identity about two-thirds of the way down the mantle. At the bottom of the mantle and in the bosh, the layers tend to mix and great care is needed to identify the marked shot. There is a region of relatively stationary coke in the center of the hearth and bosh through which the gas flows readily; for the coke bed there is relatively permeable to gas flow, particularly as the interstices between the lumps are not filled with solid particles. This region of stationary coke is also the hottest part of the furnace, because no cold material is entering it from above. The distortion of the layers of stock begins as high as the stock line; the lumps of material near the furnace wall move more rapidly than those nearer the center. The frictional effect between a lump of coke and a brick wall, laid with any care and in a reasonable state of preservation, is much less than the frictional effect of an irregular lump of coke against another lump.

In Fig. 2, it has been imagined that the coke is burned almost instantly at the nose of the tuyere; that is, the coke is supposed to be highly combustible. Here the tendency for the stock to move more rapidly along the walls is accentuated; the part of the furnace where there seems to be little movement of the charge is larger and the space through which the coke feeds down into the combustion zone is correspondingly smaller. With such a decrease in the space through which the stock descends, the time in the furnace would be shorter and the funnels, according to the analogy proposed by Van Vloten, would be smaller. Although no coke that is now in use would burn within such a short distance of the tuyeres, Fig. 2 is useful in showing more clearly the effect that localized combustion has upon the descent of the charge.

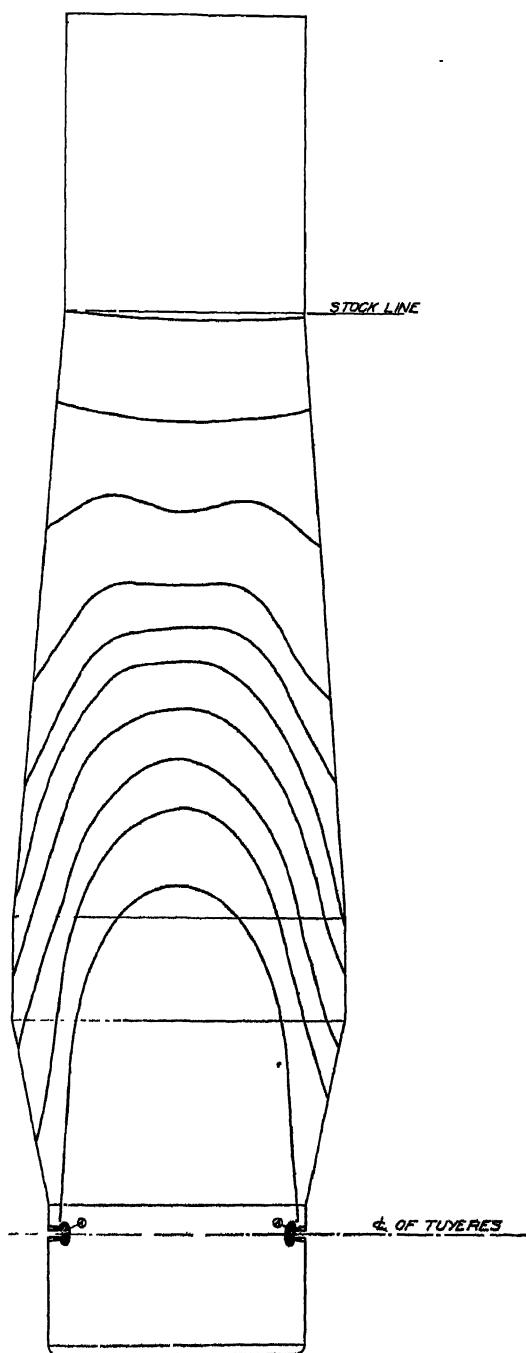


FIG. 2.—FLOW OF STOCK WHEN COMBUSTION TAKES PLACE NEAR THE TUYERES.

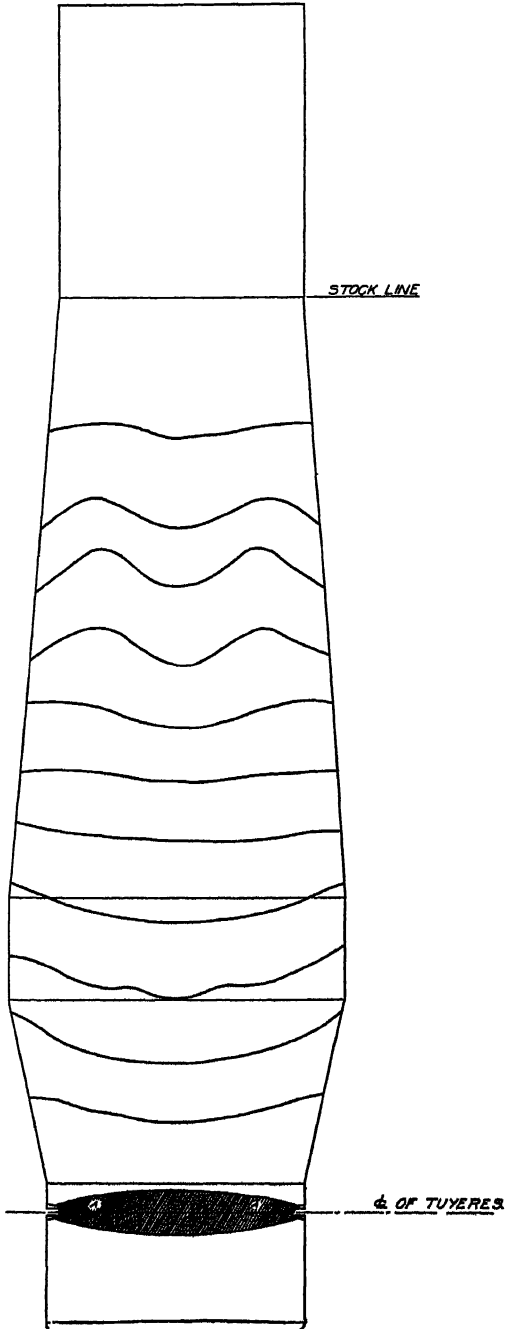


FIG. 3.—FLOW OF STOCK WHEN COMBUSTION TAKES PLACE UNIFORMLY ACROSS ENTIRE HEARTH AREA.

For comparison, Fig. 3 has been produced to show the flow of stock in a furnace when it is assumed, as Richards and Lodge did, that combustion takes place uniformly across the whole hearth area. In this case, the idle zone of the furnace has disappeared and the layers move down the furnace, retaining in general the shape taken at the stock line. Such a case is, of course, only imaginary, and in view of the large array of data collected it seems certain that when preheated air is forced into a bed of coke at temperatures of 1650° to 1800° C., the  $O_2$  will all be converted into CO within 30 to 40 in. of the entrance of the blast.

A comparison of the figures shows that a change in the space rate of combustion, which determines the positions in which coke is consumed at the tuyeres, has an effect on the movement of the stock in the blast furnace. The predominating tendency is for the coke to feed downwards into the space where combustion is taking place, which effect is transmitted as high in the furnace as the stock line. The facts here indicated are difficult to interpret in terms of practical furnace operation. In the case of a fast-burning coke, the volume occupied by the region of stationary coke in the center of the bosh cuts down the available volume of the furnace; also, as the stock near the center of the bosh is moving very slowly, it must be moving at a greater speed toward the edge of the furnace. With a normal combustion zone extending into the furnace about 30 to 40 in. from the tuyeres, it seems reasonable to suppose that lumps of coke (and calcined stone, not taken up in the fusion zone) tend to move downward near the bosh walls in the lower part of the furnace. Most of the slag and metal probably descend nearer the center of the furnace. In the upper part of the furnace, where the fine ore particles retain their identity, the resistance to gas flow would seem to be greater near the walls and more than a proportionate part of the ascending gas stream would flow through the center of the furnace. In consequence, the temperature of the fast-moving materials nearer the walls is lower, for the interchange of heat between gas and solids is reduced. The excess of solids descending through the funnel-like or cone-shaped spaces near the walls and the deficiency of gas rising through this portion of the furnace lowers the temperature of the gas and of the solids. As a result, heat loss through the walls is less and the life of the lining is lengthened.

It should be remembered that the comparison shown by Figs. 2 and 3 is between two imaginary cokes, one an extremely fast-burning coke and the other very slowly combustible. Within the range of variation in combustibility found in the furnaces investigated by Perrott and Kinney, the model experiments show no difference in the manner of stock descent.

In arranging the model experiments just described, the writers have intentionally eliminated a large number of disturbing influences. The selection of shot, in place of the irregular solids used by Richards

and Lodge, was made to isolate the effect of the location of the combustion zones from other factors such as variations in size and shape of the particles. The use of shot was suggested by the experiments of Kreisinger in his laboratory work on the drafts required to force air through fuel beds. Two sizes of lead shot were used in the model furnace; the size was found not to affect the result. The force, acting downwards on the solids, was changed by varying the angle at which the board was inclined. The magnitude of this force, when varied over wide limits, does not change the course of the materials. The use of this form of model is recommended to those interested in studying the path of materials in their furnaces. The experiments can be carried out rapidly and light can be shed on a number of problems. The effect of bosh tuyeres, such as are used abroad, can be studied quantitatively. The effect produced by removing more shot from the tuyere on one side than from the opposite can also be studied. As the purpose of the present paper is to discuss the movement of stock only in its relation to the location of the combustion zones, it is not in point to present results of such tests.

It might be thought that the results of these model tests would be made more directly applicable, and hence more valuable, if the disturbing influences that have been eliminated were left in the experiment. If these were few in number, this would undoubtedly be true; but the number of variables is so great that the necessary experiments to cover the various combinations are practically innumerable. Every furnace has its own combination of factors that determines the path of the materials. Ratio of bosh to hearth diameter, bosh angle, batter in the mantle, stock-line diameter, diameter and angle of the bell, screen analyses of the coke, stone, and ore, relative amounts of these materials charged, the presence of stickiness in those regions where the slag is first formed into a pasty semifluid mass, the mechanical force of the blast upwards through the furnace—all these factors affect one another and the resultant effect on the motion of the stock is dependent on all of them acting at once. The effect of the location of the combustion regions on the descent of the stock is probably the easiest of them all to study and the writers feel that the foregoing experiments bear directly on it and show the possibilities of the problem in a simple manner.

It was stated in the beginning that the question of how far the data collected by Perrott and Kinney go toward convincing furnace operators that cokes do not differ widely in combustibility is in doubt. It is hoped, however, that the material which has been presented will help to establish a common conception of the nature of the combustion in the blast furnace, and that some light has been shed on the probable effect of the extent of the combustion zone on the descent of the charge. In view of the fact that coke producers and furnace operators, as a whole, believe that coke combustibility plays a large part in blast-furnace opera-

tion, performance tests, either on a commercial furnace or on an experimental basis, should be conducted.

## DISCUSSION

RALPH H. SWEETSER,\* Columbus, Ohio.—At the first meeting of the Institute I attended, the Niagara Falls Meeting in 1898, the question of the size and shape of tuyeres was discussed. Among the blast-furnace men discussing the penetration of the blast were anthracite-furnace men, to whom the question of penetration was most important. They were dealing with a fuel that the ordinary blast-furnace man considers very incombustible; I was surprised, therefore, to find the Bureau of Mines men claim that anthracite is the most combustible of blast-furnace fuels, because they claim to have shown that combustion takes place on the surface of the fuel. I do not agree with them. They have confused distance of travel with speed of travel. In their report of investigations on the progress in blast-furnace research,<sup>7</sup> Royster, Joseph, and Kinney say: "The investigation has shown to the coke-oven operator the impossibility of changing coke combustibility by modifying oven practice."

In the paper under discussion, the authors, on page 224, have implicated Fieldner and Sherman in these erroneous conclusions and say "for practical purposes, the nature of the combustion of coke at the tuyeres of any furnace is constant and is affected neither by the physical properties of the coke nor by the nature of the furnace operation." They omit (that is, these men) as unimportant any tests on the combustibility of coke from their proposed methods for standard tests on coke.

These erroneous conclusions arise from the fact that the scientific investigators have a different conception of coke combustibility than have the blast-furnace men. Brassert defined coke combustibility some years ago, and said: "What principally concerns the blast furnace is the rate of progression of the combustion which depends not so much on the chemical analysis as on the physical qualities of the coal. It is this rate of progression that we term combustibility which is the speed at which the carbon molecules in the coke combine with oxygen under given conditions." That is, it is the *speed*.

I suggest this modification of Brassert's definition: "Combustibility of coke is the rate of complete gasification in front of the tuyeres of a blast furnace under standard conditions of blast temperature and of blast volume." That modification means that there is to be a certain place for the combustibility of the coke, which is in front of the tuyeres

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\* Assistant to Vice-president, American Rolling Mill Co.

<sup>7</sup> Bureau of Mines Ser. No. 2524 (September, 1923) 4.



of a blast furnace, and it is under standard conditions of blast temperature and of blast volume.

There are now no accepted standards of blast temperature and blast volume, but there must be before we can properly measure the combustibility of coke. At the bottom of p. 228, the authors say, "In Fig. 2, it has been imagined that the coke is burned almost instantly at the nose of the tuyere; that is, the coke is supposed to be highly combustible." That figure is one of the most important diagrams of blast-furnace practice. It shows exactly what takes place in the blast furnace, as far as I have been able to find out in this last year.

Just a year ago, when discussing a paper, I said that certain things could not be found out until some blast-furnace man blew off the top of his furnace. Within ten weeks, I was called to a blast furnace where the top had actually been blown off, and I looked into the interior of that furnace with the idea of getting the answer to this question of coke combustibility, and also as to where the iron ore is reduced and by what means.

The authors say that the coke is burned at the nose of the tuyere and that it is burned almost instantly; that is, the coke is supposed to be highly combustible. Perrott and Kinney<sup>8</sup> have found that coke is completely burned to CO within a comparatively short distance of the nose of the tuyere; they have proved that the distance varies only a few inches, and is between 36 and 42 inches.

Mr. Kinney conducted some experiments at the Columbus blast furnaces of The American Rolling Mill Co. last May, under full blast and also when the blowing engines were just turning over. The experiments and the analysis of the gas bore out the deductions of Perrott and Kinney at other furnaces, that the coke has been completely burned to CO within less than 40 inches.

My proposition is the modification of the Brassert definition so that coke combustibility is the speed of the coke passing from the point where it enters as solid coke to where it comes from the other end of the combustion zone completely gasified to CO.

The authors say that there is no hope for a coke-oven man to change the combustibility of the coke because they have found that this area is about the same in all blast furnaces. They might as well say that the speed of an automobile depends on how far it travels without any reference to how fast it gets across that distance. In other words, they say that this zone (shown in Fig. 1), which is unimportant in size when compared with the whole furnace, does not have anything to do with combustibility because this zone is about the same in all blast furnaces.

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<sup>8</sup> Combustion of Coke in Blast-furnace Hearth. *Trans.* (1923) 69, 543.

To find out what takes place when there is a very slow blast we ran the blowing engines just turning over after a cast and Mr. Kinney took samples of the gas across the whole area. He found that it took a little bit greater distance for the coke to be completely gasified to CO. With full blast, the CO<sub>2</sub> was practically all gone 30 in. from the tuyere, but with 1 lb. blast pressure, it was 40 in. from the tuyere before the CO<sub>2</sub> was practically all gone. If we had continued to blow that furnace on such low blast, in a short time the furnace would have been completely "stuck up;" that is why this combustion area in a well-regulated furnace will be nearly always the same.

Fig. 2, which shows very small combustion zones and the steep lines of descent along the bosh walls, is the nearest of all of the diagrams to what actually takes place in the blast furnace. It shows almost exactly the condition that I found inside the furnace that blew off its top; only I found out what had happened when this condition could not take place. The authors speak of "a cone of stationary coke in the middle of the furnace;" a friend of mine speaks of a big cone of cyanides in the middle of the furnace. I do not agree with either of them. The coke comes down along the walls, and by the time it gets through the combustion zone it is completely in the form of a gas. Several years ago, to find out the blast pressure at the center of the furnace, I had a 1/4-in. pipe driven by hand into the center of the furnace<sup>9</sup>; it was so soft in there that the pipe was easily pushed clear to the center of the hearth. It is inconceivable to think that coke would come down against that ascending stream of hot gases; the coke must come down along the walls.

The furnace that had blown off its top was a 76-ft. furnace and it blew out everything down to 34 ft. below the top. At 40 ft. down, there was a ring scaffold that left a hole only 8 ft. in diameter; that scaffold was composed entirely of iron sponge, coke, and coke breeze. The trouble had started with a bad quality coke that was not screened, and all the coke breeze had been filled into the furnace. The coke was blocky and in some cases there were chunks 12 in. cubed; it ground up easily. It was soft in places and easily went into coke breeze. This scaffold formed down along the walls to below the bosh, where the iron was in a regular funnel that was all the way around the furnace and about 3 ft. from the wall on one side and 1 ft. from the wall on the other. Between this funnel of iron and the brick of the bosh walls was the ground-up coke, coke breeze, and some lumps of coke.

Pieces of the iron scab taken along on the wall were very low in carbon but very high in sulfur, bearing out the paper that was read here last year about the iron sponge absorbing the sulfur from the coke; we found it was very high in sulfur. There was very little manganese and

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<sup>9</sup>Blast Pressure at the Tuyeres and Inside the Furnace. *Trans.* (1909) 40, 247.

very little phosphorus in the iron. Around the tuyeres, there was a great deal of spongy iron that was of about the same analysis.

A "slip" in the furnace is caused by some interruption in the regular flow of fuel down along the walls, and it is necessary for the fuel to go down through the opening that is left by the ring scaffold; after the coke that passes through that ring into the hearth is burned, the pressure goes up again and the furnace man has to slacken the blast to let more of the charge go down through the center.

Perrott and Kinney have plainly shown that the size of the combustion zone is a small part of the cubical contents of a blast furnace; the authors agree with them and so do I. But the first sentence of this paper says, "Stock descent in the blast furnace is affected by the size of the combustion zone which varies inversely with coke combustibility." I do not think that the authors mean that at all, for on p. 228, they say that when the coke burns almost instantly the stock moves faster, and they speak of a rapidly burning coke as a highly combustible coke. So I would change that definition of combustibility to mean the rate of the coke in passing from the nose of the tuyere to the end of the combustion zone.

T. L. JOSEPH.—Mr. Sweetser has defined combustibility of coke as the progressive rate of the combustion reactions that take place in the localized zones near the tuyeres under standard conditions of blast volume and blast temperature. The rate of the combustion reactions, as expressed in pounds of fuel burned per minute, depends primarily on the rate of air supply. If the blast volume remains the same, the rate of gasification in these localized zones near the tuyeres will also remain the same. If the wind is increased 20 per cent. on a furnace using coke of uniform composition, the rate of combustion will also be increased 20 per cent. Combustibility, if defined in terms of the rate of the combustion reactions, varies with the rate of air supply and not with the properties of the coke.

Combustibility, to my mind, refers to those properties of coke that determine the relative speed with which the oxygen atoms of the blast combine with the carbon of the coke. With a slow-burning coke, the oxygen will penetrate farther into the furnace before it combines with the coke. The gas analyses reported by Perrott and Kinney show, however, that the gases leaving the combustion zone in the blast furnace contain about 35 per cent. CO and 65 per cent. N<sub>2</sub>. Under these conditions, a definite weight of oxygen will combine with a fixed weight of carbon.

Differences in combustibility can be measured by the space required to complete the combustion reactions. Fast-burning coke will be consumed in a restricted area and the rate of gasification per unit volume of combustion zone will be large. A slow-burning coke will be consumed

in a larger area and the rate of gasification per unit volume of combustion zone will be smaller. It is essential, in defining combustibility, to do so in such a way as to relate it to the size of combustion zone, which changes with the character of the fuel. I agree with Perrott and Kinney who have defined combustibility as the mean rate of gasification per unit volume of the combustion zone.

I cannot agree with Mr. Sweetser's interpretation of the central portion of the furnace. If the gases from the combustion zone (about 35 per cent. CO and 65 per cent.  $N_2$ ) pass freely through this part of the furnace, it is difficult to understand how the gases withdrawn could contain as much as 75 per cent. CO.

RALPH H. SWEETSER.—Every blast-furnace man knows that a certain volume of blast is necessary to make his furnace work properly, and that if too much wind is blown into the furnace, the furnace will be overblown. Some open-hearth men will say they know that blast-furnace men do that, and that they will put oxygen into the pig iron. But it is impossible to have a blast furnace working properly if too much wind is blown into it, so that there must be a proper relation between the volume of the blast and the kind of coke that you are using.

During the War, when we had a very incombustible coke, we were obliged to cut down the volume of blast to about two-thirds of the normal volume, in order to get the furnace to drive. We could not handle the furnace any other way. Why? The coke was so hard that it would not burn properly before the tuyeres. It was blocky and high in ash; and as it was necessary to have so limy a slag there was an excess of lime above the tuyeres which united with the silica and alumina released by the burning of the coke at the tuyeres. This lime could not unite with the coke ash until the coke was burned. The coke would not burn under ordinary conditions; therefore, the combination between the volume of the blast and the combustibility of coke has to be found in each blast furnace.

RICHARD FRANCHOT, Washington, D. C.—To say that variation in the behavior of coke in the blast furnace is due to slow or fast burning is simply arriving at a conclusion by definition. This is particularly dangerous when the evidence is all against the conclusion. Since the presentation of Perrott and Kinney's paper last year, we are fairly safe in thinking that whatever causes the differences in coke behavior they are not caused by differences in the rate of burning before the tuyeres. The furnace acts differently with different cokes. To find out what it is in the coke that underlies this difference in action, it will be necessary to understand how any coke acts in the furnace. What are the factors that limit the burden-carrying capacity of the coke? This is a thermodynamic

problem, solution of which is not to be found in the literature of the blast furnace in any terms approaching mathematical precision. The outstanding fact of furnace practice, the fact that the burden is limited to less than half that which is indicated by the calorific value of the coke and the blast, has yet to be explained. And until the thermodynamic action of the coke in the furnace is satisfactorily accounted for, there will be difficulty in coming to valid conclusions as to why one coke works better than another.

SIDNEY CORNELL, New York, N. Y.—There are two rather important papers, not written by blast-furnace men, that should be taken cognizance of; one is "Combustion in Fuel Beds" by Kreisger and others, and the other is by Sherman and Blizard.<sup>10</sup> These papers are in connection with combustion of coal, but my observation is that in the blast furnace the gases formed have a dampening effect on the combustibility of the coke. These gases will run 13 per cent.  $\text{CO}_2$  at the top, gases formed in a boiler will run 16 per cent.  $\text{CO}_2$ . What is the dampening effect by formation of  $\text{CO}_2$ ? It may be 3 per cent. at the tuyeres; that is the subject these gas men should study when they make their analysis.

RALPH H. SWEETSER.—The authors have said that the coke-oven men cannot change the combustibility. I have a double job with The American Rolling Mill Co.—I am located at one of the blast-furnace plants and I am also one of the officials in the byproduct coke company, which is located in another city. If the furnace is working all right, the blast-furnace men are contented. If it is not working all right, they at once want the coke-oven man to change the combustibility of the coke. The authors have said the coke-oven man cannot do it, but it has been done. The coke-oven men have some control over the combustibility of their coke.

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<sup>10</sup> Combustion of Blast-furnace Cokes in Fuel Beds. *Trans.* (1923) 69, 526.

## Use of Sodium Picrate in Revealing Dendritic Segregation in Iron Alloys

BY ALBERT SAUVEUR, S. D., AND V. N. KRIVOBOK, MET. E., CAMBRIDGE, MASS.

(New York Meeting, February, 1924)

IRON, like other metals, solidifies through the formation of dendritic crystals; iron alloys forming solid solutions, like other solid solutions, solidify likewise through the formation of dendritic crystals. The alloying elements or impurities as well as the inclusions segregate generally in the interstices, or "fillings," between the axes and branches of the dendrites; that is, in the portions last to solidify. This results in dendritic segregation or heterogeneity, which is generally persistent and makes possible the revelation of the dendritic crystallization of the metal through the selective action of a suitable etching reagent.<sup>1</sup> For this purpose, a cupric solution, such as Le Chatelier's, is generally used, copper being deposited on the pure, or relatively pure, ferrite present in the axes while the fillings remain free, or relatively free, from copper deposition. The dendritic structure, formed on solidification in a steel containing 0.50 per cent. carbon, 0.37 per cent. manganese, 0.12 per cent. silicon, 0.07 per cent. sulfur, and 0.035 per cent. phosphorus is shown, after treatment with Le Chatelier reagent, in Fig. 1 under a magnification of 8 diameters.

Commercial steel always contains inclusions of manganese sulfide, which are located in the fillings of the dendrites. Comstock has shown that boiling sodium picrate imparts a dark coloration to these inclusions. We find that this reagent likewise reveals dendritic segregations in commercial steel, as shown in Fig. 2, under a magnification of 8 diameters, which represents the same spot as that shown in Fig. 1. The fillings have been darkened while the axes remain white, the action being, therefore, the reverse of that of cupric reagents. On closer examination, under higher magnification (Fig. 3) it is found that the picrate blackens the small particles of manganese sulfide, that these are frequently surrounded by a rim of white, or relatively white, ferrite, and that both the ferrite

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<sup>1</sup> The formation of dendrites resulting in permanent dendritic segregation and its detection has been described at some lengths by one of the authors—Albert Sauveur: *Crystallization of Iron and its Alloys*. *Trans. Am. Soc. for Steel Treating* (1913) 4, 12.



FIG. 1.—COMMERCIAL HYPOEUTECTOID ETCHED WITH LECHATELIER CUPRIC REAGENT;  
VERTICAL ILLUMINATION.  $\times 8$ .

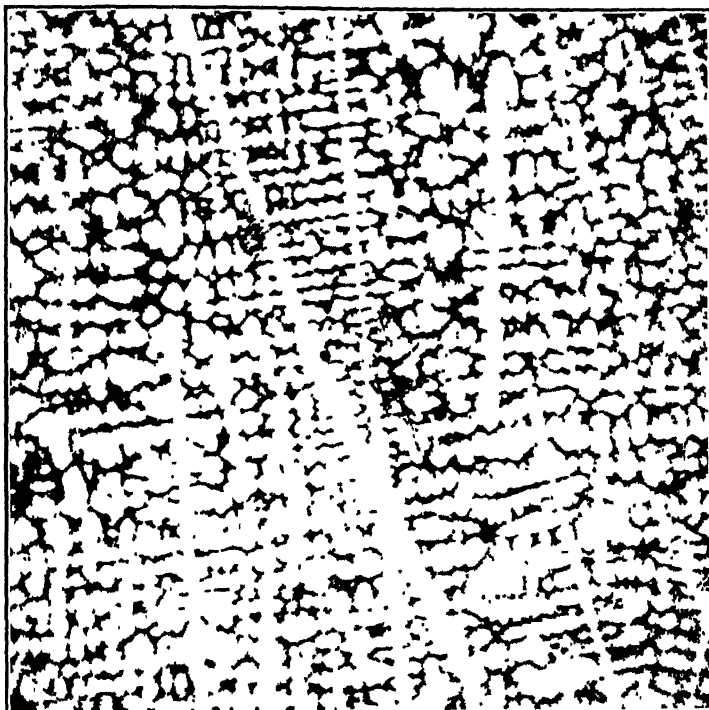


FIG. 2.—SAME SPOT AS THAT SHOWN IN FIG. 1 ETCHED WITH BOILING SODIUM PICRATE;  
VERTICAL ILLUMINATION.  $\times 8$ .



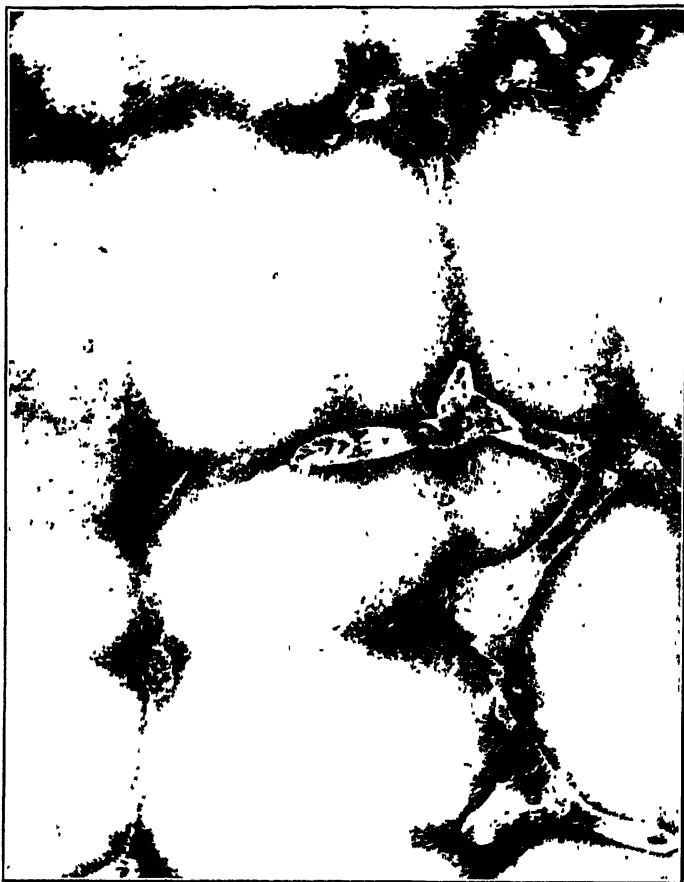


FIG. 3.—COMMERCIAL HYPOEUTECTOID STEEL ETCHED WITH BOILING SODIUM PICRATE.  
× 100.



FIG. 4.—HYPOEUTECTOID COMMERCIAL STEEL ETCHED WITH BOILING SODIUM PICRATE.  
× 750.



FIG. 5.—EUTECTOID STEEL ETCHED WITH BOILING SODIUM PICRATE.  $\times 1000$ .

and the cementite in the pearlite surrounding the ferrite rims are blackened by the picrate. This results in a solid black appearance, under low magnifications, being imparted by sodium picrate to the fillings, sharply differentiating them from the white axes (Fig. 2). If the minute particles of manganese sulfide only were darkened by the picrate, dendritic segregation could not generally be revealed by this reagent. The mechanism of the action of picrate is shown under higher magnification, in Fig. 4. The darkening by picrate of the pearlite surrounding manganese-sulfide inclusions is further illustrated in Fig. 5, in the case of a eutectoid steel. The absence of free ferrite in this steel may account for the absence of ferrite rims surrounding the inclusions.

In Figs. 6, 7, and 8, the same spot in a hypoeutectoid steel has been photographed under a magnification of 100 diameters, respectively unetched, etched with nitric acid, and etched with sodium picrate. It is to be noted that etching with nitric acid leaves the inclusions surrounded by uncolored ferrite, while the pearlite is uniformly colored, there being no selective action between the pearlite in the fillings and the pearlite in the axes, hence no revelation of dendritic structure.

Etching with sodium picrate, on the contrary, causes the pearlite surrounding the inclusions and their ferrite rims, that is the pearlite in the fillings, to be colored dark while the pearlite in the axes remains uncolored, resulting in the revelation of a dendritic crystallization (Fig. 2).

The possibility of revealing persistent dendritic segregation in ordinary commercial steel by the use of sodium picrate seems to depend, therefore, on the presence of manganese-sulfide inclusions and hence of both manganese and sulfur in the steel. To verify the correctness of this conclusion, a steel free from manganese and sulfur was prepared by melting electrolytic iron with sugar charcoal; it contained 0.36 per cent. carbon. Dendritic segregation was revealed by etching with the cupric reagent (Fig. 9), while treatment with sodium picrate failed to disclose it.

A pure alloy of iron and manganese was also prepared; it was found that neither treatment with the cupric reagent nor with sodium picrate resulted in bringing out a dendritic structure, from which it may be concluded that manganese alone does not cause persistent dendritic segregation or that, if segregation is caused, it cannot be revealed by the reagents employed.

Etching, with sodium picrate, cast manganese steel containing about 12 per cent. manganese and 1 per cent. carbon brings out clearly the existence of persistent dendritic segregation (Fig. 10). As is usual with manganese steel, the dendrites formed on solidification are comparatively very small and a considerably higher magnification is generally required to reveal them. Fig. 10 is magnified 50 diameters. The fillings have been darkened while the axes remain light in color. We believe the

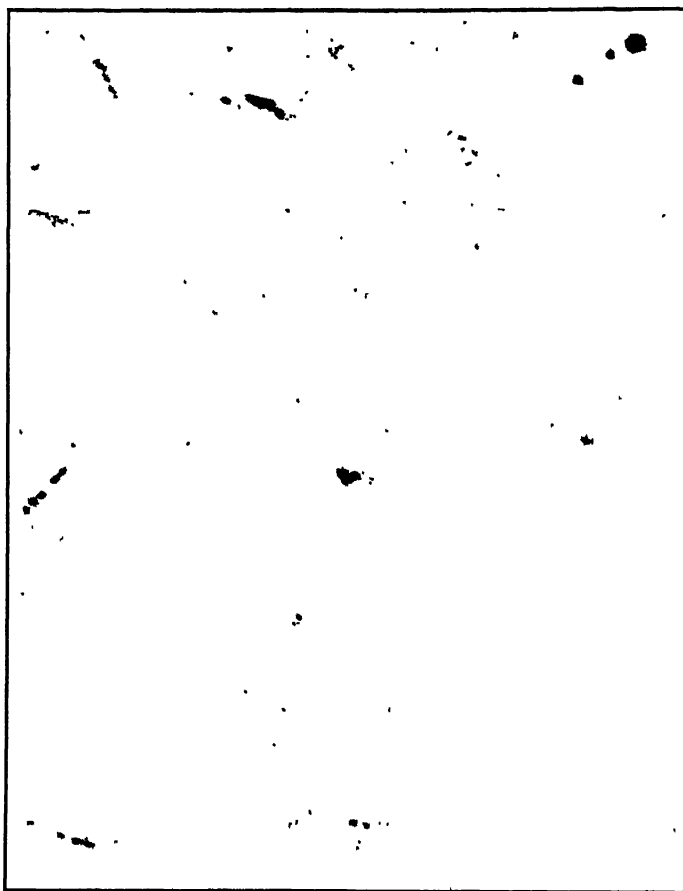


FIG. 6.—SAME SPOT HYPOEUTECTOID STEEL AS THAT SHOWN IN FIGS. 7 AND 8,  
UNETCHED.  $\times 100$ .



FIG. 7.—SAME SPOT HYPOEUTECTOID STEEL AS THAT SHOWN IN FIGS. 6 AND 8, ETCHED WITH NITRIC ACID.  $\times 100$ .



FIG. 8.—SAME SPOT HYPOEUTECTOID STEEL AS THAT SHOWN IN FIGS. 6 AND 7, ETCHED WITH BOILING SODIUM PICRATE.  $\times 100$ .

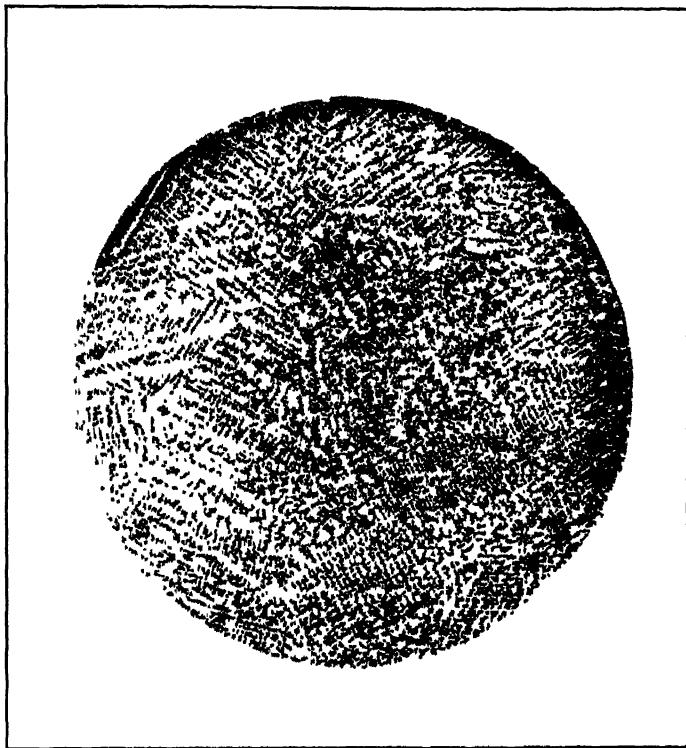


FIG. 9.—ELECTROLYTIC IRON AND SUGAR CHARCOAL MELTED IN VACUUM; CARBON 0.36 PER CENT.; ETCHED WITH LE CHATELIER REAGENT; OBLIQUE ILLUMINATION.  $\times 4$ .



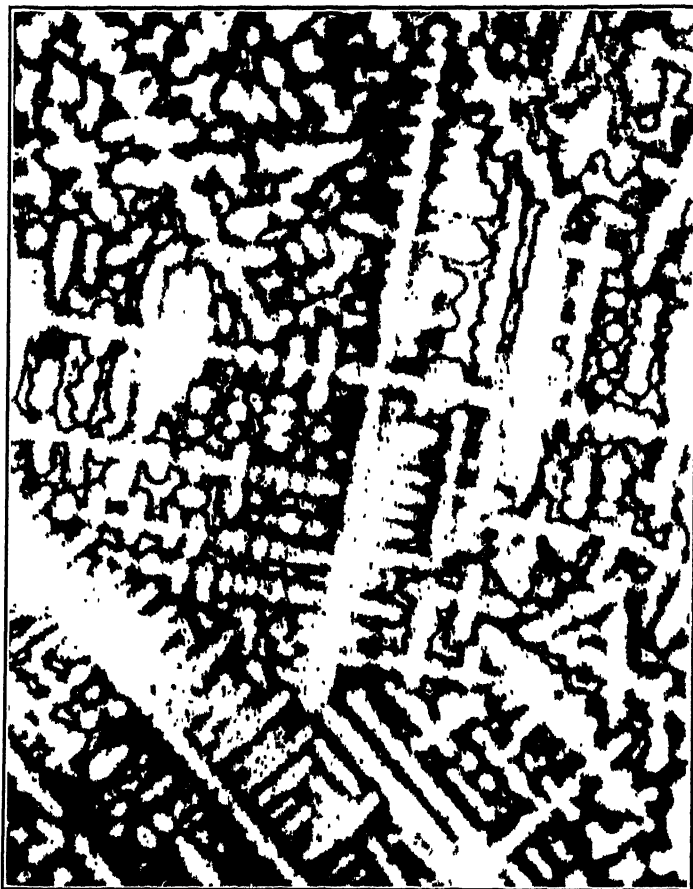


FIG. 10.—MANGANESE STEEL, ETCHED WITH BOILING SODIUM PICRATE.  $\times 50$ .

darkening of the fillings to be due chiefly to the action of the picrate reagent on the free carbides, which necessarily have segregated in the fillings, rather than to the presence of manganese-sulfide inclusions.

Summing up: boiling sodium picrate has been found a useful reagent in disclosing persistent dendritic segregation in commercial steel. The mechanism of the action has been explained. It also reveals persistent dendritic segregation in cast manganese (austenitic) steel.

## DISCUSSION

GEORGE F. COMSTOCK, Niagara Falls, N. Y. (written discussion).—The authors have shown some interesting instances where etching with the sodium picrate reagent was successful in giving a clear picture of the distribution of certain impurities in steel. They do not seem to have shown, however, that this method is any better than the methods of etching with cupric-chloride reagents, as developed by Stead and Le Chatelier. Stead, for instance, proved that his reagent differentiated between parts of a steel specimen that were comparatively pure and other parts more contaminated by the segregation of phosphorus and other impurities in solid solution. The authors have not demonstrated any such action by the reagent they advocate, and indeed seem to admit that it does not act in this way. It attacks the sulfide inclusions and darkens the steel around them, thus showing, not dendritic segregation in general, but merely the sulfide distribution. As a macrographic reagent for this purpose, the method is undoubtedly of value, in cases where sulfur printing is not desirable.

The writer has often noticed the darkening or corrosive action of the boiling alkaline sodium picrate on the steel surrounding the sulfide inclusions that were eaten away by this etching, but has considered it a disadvantage of the method, which should be avoided as far as possible. The authors, however, have shown how this action may be made use of. It would be interesting to know if they consider the action anything more than a pitting effect, or corrosion, possibly electrochemical, due to the contact between sulfide and steel where the inclusions are present. The authors should state how long they boil their specimens in the reagent to obtain such clear results as are shown in Figs. 2 and 8.

In our laboratory, very little trouble has been experienced in showing dendritic segregation by means of Stead's reagent, which has been found entirely satisfactory for this purpose. It is made up by dissolving 1 gm. cupric chloride and 4 gm. magnesium chloride in 20 c.c. water and 1 c.c. concentrated hydrochloric acid, and then adding 100 c.c. absolute alcohol. Etching with this reagent takes about a minute and it does not require heating. Its effect may be made more contrasty by continuing the application until an appreciable film of copper is deposited, and then

wiping off the copper with a piece of cotton soaked in ammonia. This method is particularly useful for magnifications around 20 or 50 diameters. Humfrey's method<sup>2</sup> of "macro-etching" with copper-ammonium chloride solutions of varied acidity also gives excellent results for very low magnifications. It does not appear from the paper that the method advocated by the authors is any improvement over these older methods for revealing dendritic segregation in steel.

JOHN H. HALL, Highbridge, N. J. (written discussion).—Probably no subject is of greater interest to metallographists than that of dendritic segregation and the work of the authors is most welcome in shedding additional light on this important subject. The simple method of revealing dendritic segregation described in this paper will be of the greatest value to all of us and the sample of manganese steel shown in Fig. 10 is of particular interest to myself.

It is not clear to me just what, in the authors' opinion, causes the darkening of the pearlite in ordinary carbon steel surrounding the inclusions of manganese sulfide or the free ferrite, as the case may be. In a general way, it seems to be indicated that the carbon in the darkened portions is somewhat higher than in those portions of the pearlite that are not blackened by the sodium picrate.

In the case of the manganese steel shown in Fig. 10, the heat treatment that this sample has received is not indicated; a micrograph of the same sample etched with nitric acid would have been of value and interest as it would indicate the presence or absence of what we usually understand as free carbide in the microstructure. We have, in our records, many specimens of cast manganese steel, either in the cast state or not, so treated as to cause the free carbide to be absorbed in the austenite ground-mass, which show a pronounced dendritic arrangement of the free carbide. In samples of this steel, however, that have been heated to about 1060° and quenched in water, free carbide is not present in the microstructure, as revealed by nitric acid etching, the structure consisting simply of crystals or grains of austenite. We have long noticed indications of non-uniformity in these austenite crystals, which are difficult to describe in words. Within the last year Professor Sauveur's papers on dendritic segregation have drawn our attention to this subject and we have begun some investigations, which as yet are not far enough advanced to justify us in drawing any conclusions. Our opinion, however, is that when dendritic segregation is found in a sample of manganese steel that shows simply austenite crystals on etching with nitric acid, the dendrites are due to the fact that the carbon has not been uniformly diffused in the austenite before quenching the steel to fix the austenitic condition. In particular,

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<sup>2</sup> Iron and Steel Inst. *Jnl.* (1919) 99, 273.

we do not believe that phosphorus is responsible for it, as we found no traces of dendritic segregation in a sample of manganese steel specially prepared containing about 0.275 per cent. phosphorus.

We have a sample of manganese steel made by the thermit process containing about 10 per cent. manganese and 0.80 per cent. carbon, which has been heated to about 1000° C. and quenched in water. After nitric-acid etching, it shows simply pure austenite crystals, which, of course, are very large owing to the high temperature at which the metal was poured. After etching with suitable reagents, this sample shows dendritic segregation on so large a scale that it is best observed with an ordinary magnifying glass rather than with the microscope.

The existence and persistence of dendritic segregation in many samples of steel has been shown often enough to convince us all that we should go into the subject very thoroughly. What seems to be lacking so far is convincing data to show the effect of dendritic segregation on the physical properties of the metal. To my mind, most of the efforts so far made in this line have not definitely proved the relation between dendritic segregation and physical properties, and I personally hope that Professor Sauveur will, in the next few years, contribute information along this line.

■

## Micrographic Detection of Carbides in Ferrous Alloys

BY NORMAN B. PILLING,\* EAST PITTSBURGH, PA.

(New York Meeting, February, 1924)

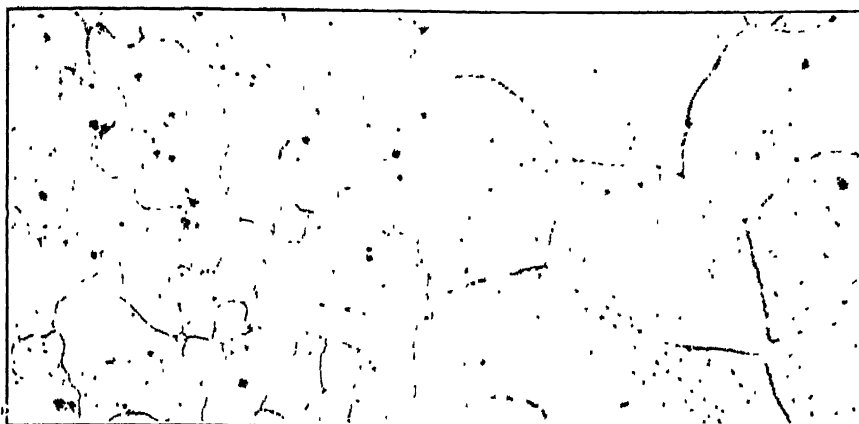
THE technical difficulties hampering the metallographic analysis of silicon steels are chiefly the result of the extreme corrodibility of these alloys. The addition of silicon to iron in increasing quantities, up to about 6 per cent., rapidly increases the susceptibility of the alloy to chemical attack, not only in acid solution, but in water. This renders the preparation of metallographic sections very difficult, because of a non-selective attack upon the finely polished surface by the water used as a lubricant in polishing. This water attack masks the true structural details revealed by suitable etching reagents. It is thus necessary to use alcohol as a polishing lubricant in the last stages of preparation and to avoid all etching reagents having an aqueous base.

A specific reagent for the identification of iron carbide in ferrous alloys, and the one hitherto used almost exclusively by metallurgists, is an alkaline aqueous solution of sodium picrate, which stains this constituent selectively. Its application to silicon steels has not proved successful, as its distinctive selective action is more or less completely hidden by the general attack of the aqueous solvent on the silico-ferrite, greatly accentuated by the fact that this reagent must be used at its boiling temperature (105° C.). Thus, a powerful metallographic aid to the study of the higher silicon alloys, such as transformer steels, is lost. A new reagent has been developed for the purpose of overcoming this difficulty. It is with some hesitation that the list of etching reagents, already overburdened, is increased, but the properties of this new reagent are advantageous in several ways and a definite field for it may be found in the metallography of ferrous alloys.

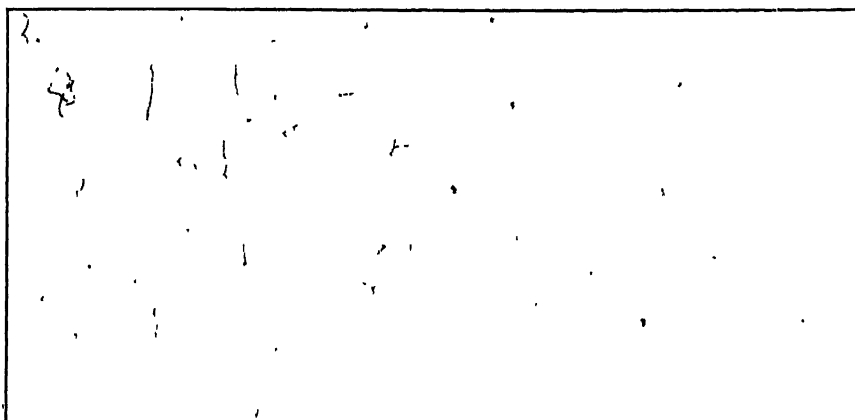
The reagent consists of a dilute solution of nitric acid and methyl alcohol in nitrobenzol. It is a great advantage to secure an anhydrous solution, as a tendency toward acidic etching has been traced to small amounts of water. A convenient method of preparation is to make an anhydrous stock solution of nitric acid in methyl alcohol in the proportion 20 per cent. acid by weight (12.5 per cent. by volume). The alcohol can

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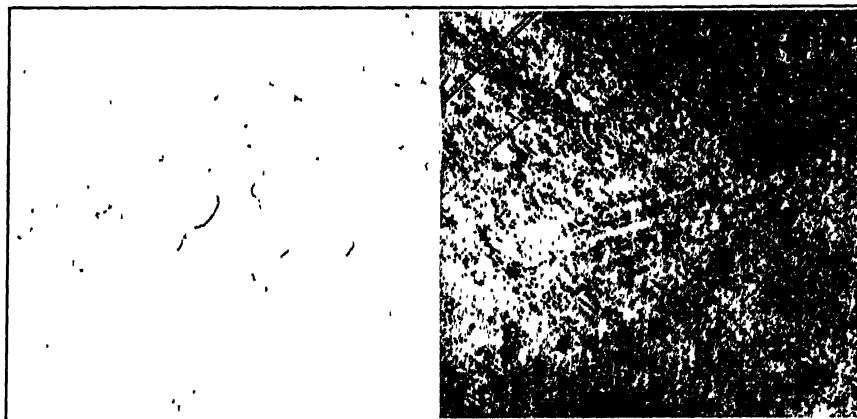
\* Metallurgist, Westinghouse Elec. & Mfg. Co.



(a) ETCHED WITH ALCOHOLIC NITRIC ACID.



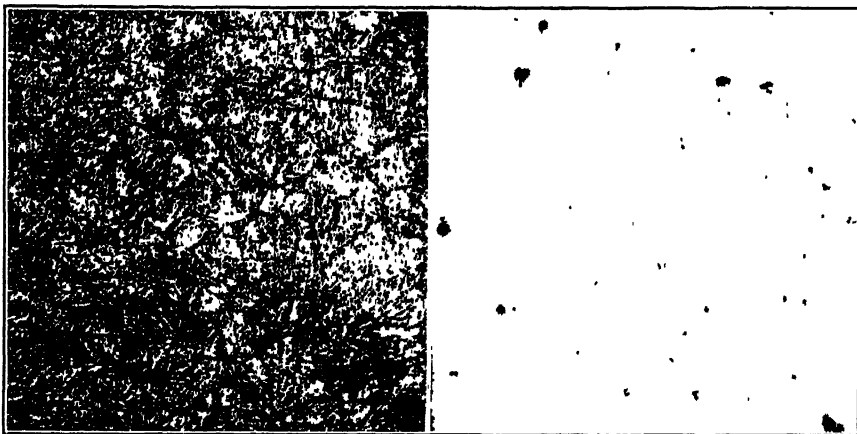
(b) ETCHED WITH NITROBENZOL REAGENT.



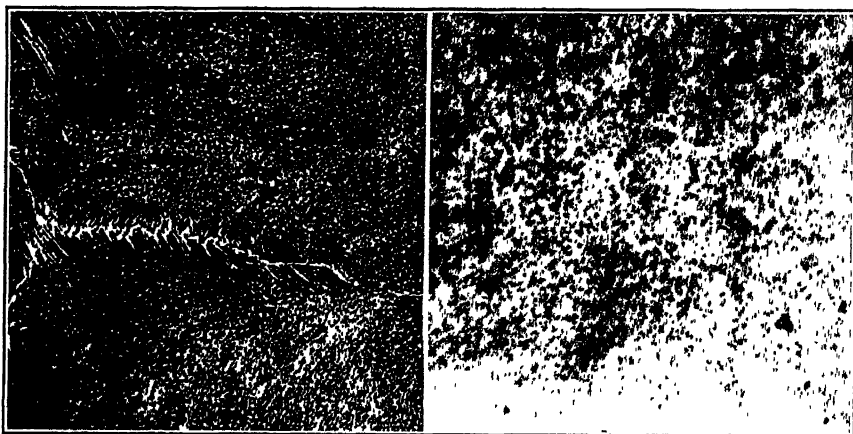
(c) ETCHED WITH SODIUM PICRATE.

FIG. 1.—LOW-CARBON IRON, C = 0.015 PER CENT. FIG. 2.—3.5 PER CENT. SILICON STEEL, C = 0.015 PER CENT.  $\times 100$ .

be dehydrated sufficiently by distillation over quicklime. Anhydrous acid can be prepared by distillation from a mixture of dry  $\text{NaNO}_3$  in concentrated sulfuric acid, but fuming nitric acid does as well. The etching reagent is then made by adding 40 drops of this solution to 50



(a) ETCHED WITH ALCOHOLIC NITRIC ACID. (b) ETCHED WITH NITROBENZOL REAGENT.  
FIG. 3.—MARTENSITIC CARBON STEEL.  $\times 100$ .



(a)  $\times 100$ .

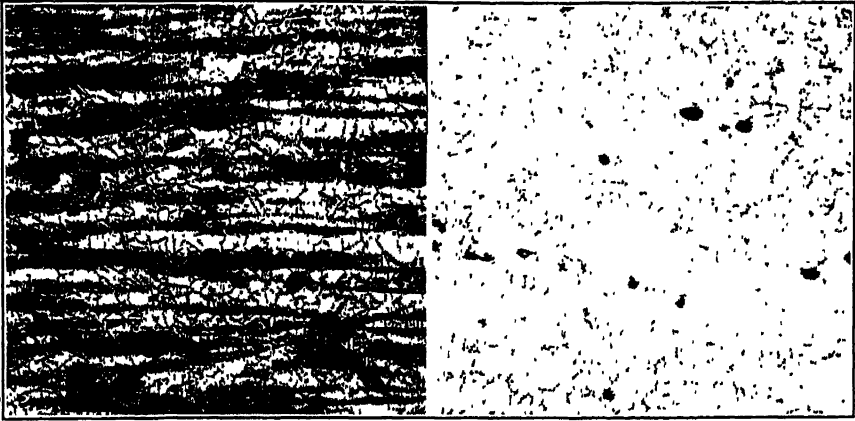
(b)  $\times 1000$ .

FIG. 4.—CARBIDIC MARTENSITE, ETCHED WITH NITROBENZOL REAGENT.

c.c. nitrobenzol. Stored in dark-colored bottles, it will keep for several months. Etching is accomplished by simple immersion in the fluid; about 20 seconds action is required for the strength of solution given. At the same time a thin, very tenacious film of an insoluble organic iron compound is deposited over the entire surface; after rinsing in alcohol, this can be removed by swabbing with concentrated sodium-hydroxide

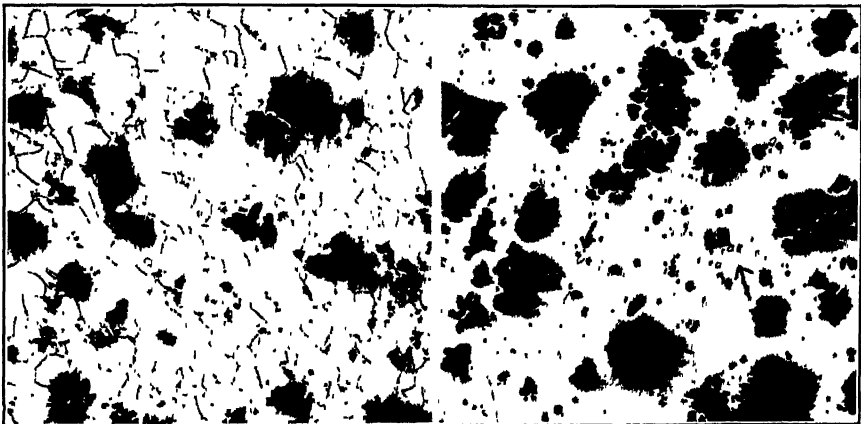
solution. The sodium hydroxide is, in turn, removed by rinsing with either alcohol or water, as the properties of the alloy demand.

The characteristic action of this reagent is a selective attack upon structurally free iron carbide, leaving the matrix (ferrite, martensite, or austenite) unattacked. It differs from sodium picrate in that the carbide



(a) ETCHED WITH ALCOHOLIC NITRIC ACID. (b) ETCHED WITH NITROBENZOL REAGENT.

FIG. 5.—AUSTENITIC MANGANESE STEEL.  $\times 100$ .



(a) ETCHED WITH ALCOHOLIC NITRIC ACID. (b) ETCHED WITH NITROBENZOL REAGENT.

FIG. 6.—MALLEABILIZED CAST IRON.  $\times 100$ .

is etched without persistent and deep-seated staining and the operation is conducted in a cold solution.

The use of the nitrobenzol reagent is illustrated in the accompanying photomicrographs. Fig. 1 shows a pure iron-carbon alloy and Fig. 2 a pure iron-carbon-silicon alloy, both of which contain 0.015 per cent.



carbon. This carbon is present as minute films of carbide forming partial envelopes around the ferrite grains. Figs. 1(a) and 2(a) show these two alloys etched with an alcohol solution of nitric acid (10 per cent.) and are typical examples of the structural resolution afforded by acid-etching reagents. The characteristic of this type of etching is differentiation of the crystalline grains and the presence of minute quantities of a second phase at the intercrystalline zone may be almost wholly masked by the superimposed development of grain boundaries. The uniformly dotted appearance of the interior of the grains in the silicon-steel photomicrograph [Fig. 2(a)] is due to an incipient water attack caused by the small amount of water associated with acid. Figs. 1(b) and 2(b) are the same alloys etched with the new nitrobenzol reagent; in this case, the grain detail is entirely absent and the presence of the carbide films is shown with emphasis. Figs. 1(c) and 2(c) are the same two alloys etched with alkaline sodium picrate. The identification of the constituent in the iron-carbon alloy revealed by the nitrobenzol reagent is now confirmed by its analogous reaction with sodium picrate [Figs. 1(b) and (c)]. The failure of the silicon steel to respond satisfactorily to this reagent is shown in Fig. 2(c); the whole metallic surface has been attacked and evidence of the presence of carbides is lost in a maze of spurious detail.

Several classes of carbide-bearing alloys, etched comparatively with alcoholic nitric acid and nitrobenzol reagent are shown in Figs. 3 to 6. Figs. 3(a) and (b) were taken from a high-carbon martensitic steel containing a very small amount of troostite and free from coalesced carbide. Troostite etches darkly, but not so intensely as with acid reagents. Martensite seems not to be entirely inert, but etches extremely slowly. In (b) traces of troostite are indicated at the boundaries of the polyhedral grains. Fig. 4(a) shows a dark etching martensite (with massive carbide) which proves, under high magnification, to contain a host of highly dispersed carbide particles, Fig. 4(b).

Figs. 5(a) and (b) represent an austenitic manganese steel of the type used in making military helmets. The banded appearance brought out by the acid etch is due to segregation of manganese in solid solution; the nitrobenzol etch ignores this condition and discloses the carbide network exclusively.

Figs. 6(a) and (b) were taken from a malleableized-iron casting and show the possibility of detecting, micrographically, very small amounts of combined carbon in the presence of a large total carbon content. This would have been very difficult with sodium picrate, as the darkly stained carbides would have been indistinguishable from the many flecks of temper carbon.

## Simulating Natural Light in Metallography

BY H. S. GEORGE,\* MET. E., LONG ISLAND CITY, N. Y.

(New York Meeting, February, 1924)

ON ONE occasion when it seemed desirable to reveal under the microscope not only the metallic structure of an alloy, but certain small non-metallic inclusions that are ordinarily obliterated by etching, it was discovered that, by partly eclipsing the illuminating pencil of light rays, the residual light was thrown on the object from one side and the structure was brought out in relief. At the same time, the non-metallic inclusions were retained in clear view.

In this first demonstration of lighting obliquely through the objective a card was thrust part way into the light beam between the arc iris and the light filter; the shadow of the card on the filter served to locate its position. Next several stiff-paper disks of various diameters were mounted on flexible wires; some plasticine on the other end of the wires made it easy to adjust and maintain a disk at any desired position in the light beam. To facilitate manipulation, an assortment of disks was mounted on a wheel, as shown in Fig. 1.

The purpose of partly eclipsing the light beam was discussed in an earlier paper.<sup>1</sup> There it was pointed out that the usual methods of illuminating opaque objects for microscopic examination lend an unnatural appearance to the view, while the new method, which has been termed conical illumination, reveals the true relationship of constituents by simulating natural lighting.

In nature, all objects are lighted diffusely, or by light predominating from one direction, or by a combination of diffuse and directed light. Under these conditions, objects appear to have three dimensions—they possess relief. The kind of illumination known to metallographists as vertical or axial results in an unnatural appearance, as a large proportion of the illuminating rays are parallel to the line connecting the eye with the object, a condition almost never met in nature. Microconstituents

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\* Metallurgist, Union Carbide & Carbon Research Laboratory.

<sup>1</sup> H. S. George: Conical Illumination in Metallography. *Trans. Am. Soc. for Steel Treating* (1923) 4, 140.

that really stand in relief, or are depressed, seem to be flat because of this unnatural lighting, which produces no high lights or shadows. The result is that the metallographist interprets appearances as best he can.

The characteristic representation of etching pits in the textbooks is an example of erroneous interpretation—the little triangles and squares are shown in outline as they appear under the microscope and are assumed to be pits that have been etched out. The writer recently examined, under conical illumination, a specimen of Armco iron, after

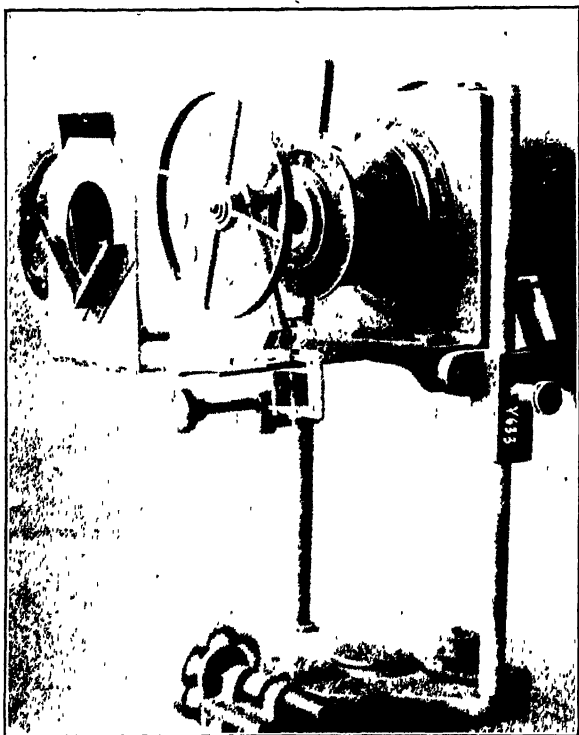


FIG. 1.—DEVICE FOR OBTAINING CONICAL ILLUMINATION.

etching, and was surprised to see that the pits were really pyramids; this is shown in Figs. 2 to 5. In these, the disk was manipulated so as to light the field from four directions in turn, the position of the disk being referred to as at 12 o'clock, 3 o'clock, etc. This method of denoting the position of the disk will be explained later. The direction of lighting is indicated in each case, thus showing definitely that the corners of the cubic units composing the grain actually project. If any or all of these views give the impression of being pits, this is an optical illusion that may be destroyed by a process of reasoning with the known direction

of lighting as a basis. This illusion, which sometimes presents itself in views lighted by conical illumination, was discussed at some length in the previous article. It should be constantly watched for and guarded against.

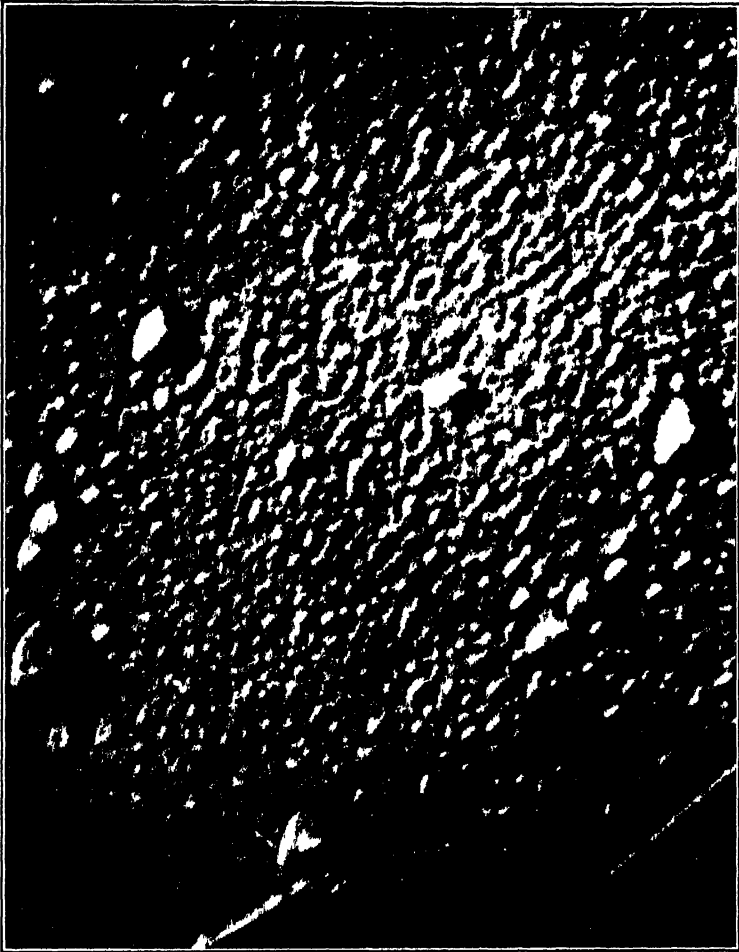


FIG. 2.—PHOTOMICROGRAPH OF ARMCO IRON UNDER CONICAL ILLUMINATION, SHOWS THAT ETCHING PITS ARE REALLY PYRAMIDS; LIGHT IS FROM LEFT TO RIGHT.  $\times 2000$ .

It has been stated that so-called "vertical" or "axial" illumination produces unnatural effects. The terms vertical and axial convey an incorrect idea of the nature of the light pencil. The bundle of rays, especially in that section of the pencil between the objective lens and

the object, really is conical in shape and only the one ray coinciding with the axis of the cone is actually vertical, or axial. The rest are oblique. Practically speaking, there is an inner bundle of rays sufficiently axial in character to be so considered and an enveloping bundle whose limiting

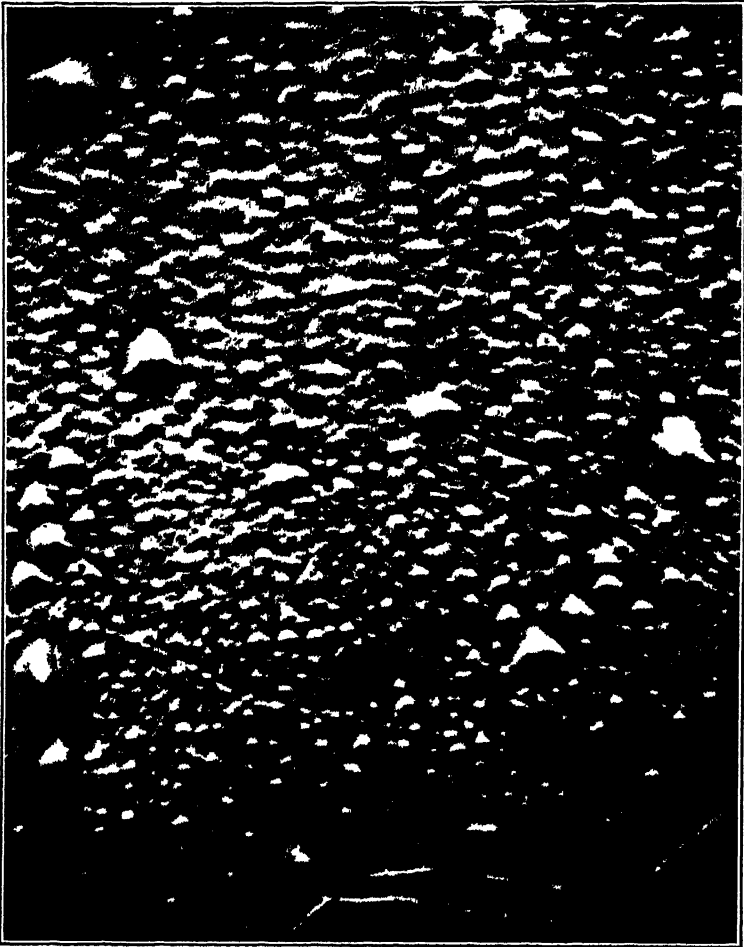


FIG. 3.—SAME FIELD AS IN FIG. 2, WITH LIGHT DIRECTED FROM ABOVE.

obliquity is fixed by the numerical aperture of the objective. But the axial rays mask the effect of the oblique rays. Stopping out the axial rays by interposing an opaque disk in their path allows the outer rays full scope to produce natural effects.

Fig. 6 illustrates, diagrammatically, the composite nature of so-called vertical or axial light. The diagram represents, in simplified form, an

inverted microscope with reflecting disk, prism, and eyepiece omitted. Fig. 7 indicates the method of producing conical illumination by stopping out the central portion of the beam, although in practice the interposed disk is set eccentrically to simulate natural light. Fig. 10, position 3, shows the shadow of the disk on the light filter in a typical working

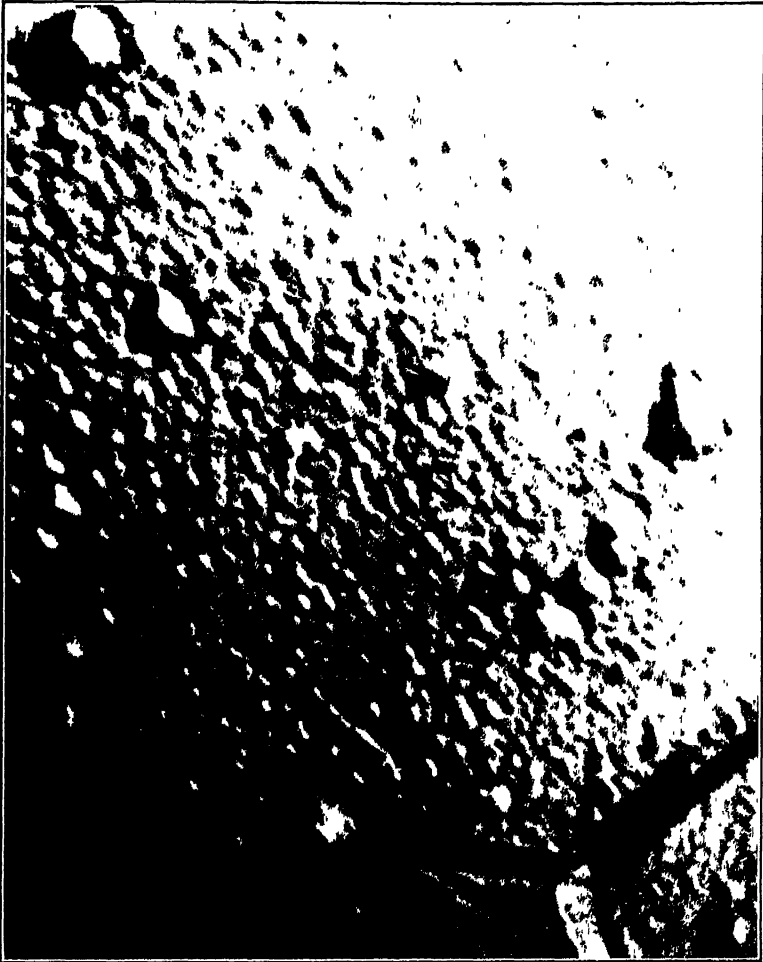


FIG. 4.—SAME AS FIG. 2, WITH LIGHT DIRECTED FROM THE RIGHT.

position; all the central and most of the oblique rays on one side are eclipsed. The two horns of the light crescent serve to produce the softening effect of diffused light, which is almost always present, to a certain extent, in nature in combination with a strong directed light. Considerable flexibility of lighting is attainable by manipulating the stop

and changing its size; in this way almost any desired degree of contrast, shading, and relief can be brought out.

The greater the power of the objective, that is, the larger its numerical aperture, the more oblique are the extreme rays in the enveloping zone and the more adapted it is to manipulation for bringing out any

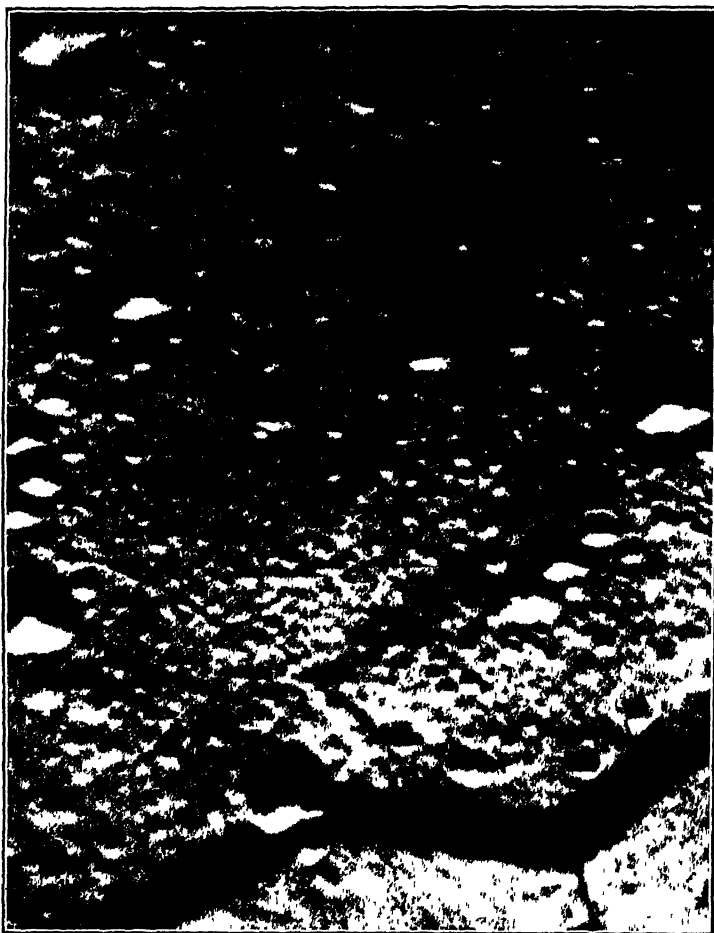


FIG. 5.—SAME AS FIG. 2, WITH LIGHT DIRECTED FROM BELOW.

desired amount of relief. This does not mean that relief cannot be brought out with the lower power lenses. Resolving power and the ability to bring out natural relief are determined by the degree of obliquity in the cone of rays between the objective and object and, with a lens of sufficient power to delineate clearly a constituent, there is enough obliquity to bring out relief in that constituent—if it has relief.

In the preceding paper, little in the way of definite procedure was given. It is still too early to formulate a strict technique and what is given here should be considered as merely tentative. The writer has derived much satisfaction from the method and finds increasing use for it; in fact, all of his microscopic studies and photomicrographs are made with its aid, even on materials that show little or no relief. There would seem to be every reason to utilize a more natural method of illumination and

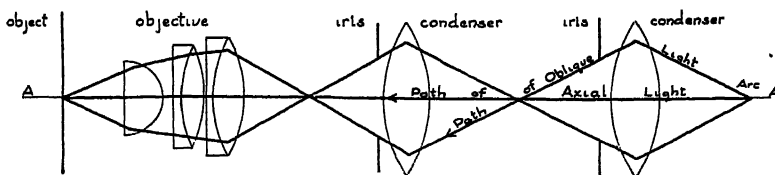


FIG. 6.—PATH OF LIGHT IN METALLOGRAPHIC MICROSCOPE USING VERTICAL ILLUMINATION, SHOWING COMPOSITE NATURE OF THE LIGHT PENCIL.

the fact that no relief is manifested may have much significance, especially for purposes of record, as in photomicrographs.

While the value of the method is more apparent in cases where there is relief, where the difference between photomicrographs taken with the two systems of illumination can be readily seen, it may be of vital significance to know that there is no relief rather than to wonder what the appearance would have been had conical light been utilized; for this reason the desirability of always photographing with conical light is

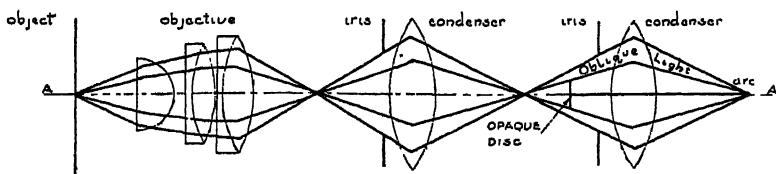


FIG. 7.—PATH OF LIGHT IN METALLOGRAPHIC MICROSCOPE USING CONICAL ILLUMINATION; AXIAL PORTION OF LIGHT PENCIL STOPPED OUT BY AN OPAQUE DISK.

strongly emphasized. There does not seem to be the slightest reason why the method should not become universal for microscopic examination of opaque materials and the requirements of metallography, at least, argue strongly for a more natural method of lighting.

Few, if any, metallographic surfaces are perfectly plane but it is necessary to use high powers to reveal surface inequalities in many cases. Some materials, however, show marked relief even at low powers. A good illustration of this is given, in Fig. 8, of a copper-chromium alloy. The hard dendrites of excess chromium have been polished in relief above the softer copper-rich matrix; Fig. 9 shows a portion of the same field under vertical illumination.





FIG. 8.—USE OF CONICAL ILLUMINATION IN LOW-POWER WORK; COPPER-CHROMIUM ALLOY (CAST) UNETCHED; 16 MM. OBJECTIVE;  $\times 250$ .

Specific directions as to proper iris opening, size of spot, and degree and direction of eccentricity of spot cannot be given because these depend on the objective used, amount of relief present, shape and arrangement of constituents, and orientation of the specimen. Correct combinations are found by trial. The procedure may be as follows:

A preliminary examination in the ordinary manner should be made, tentatively introducing a stop from time to time with each objective. Any relief present will be evident at once, in most instances. If it is

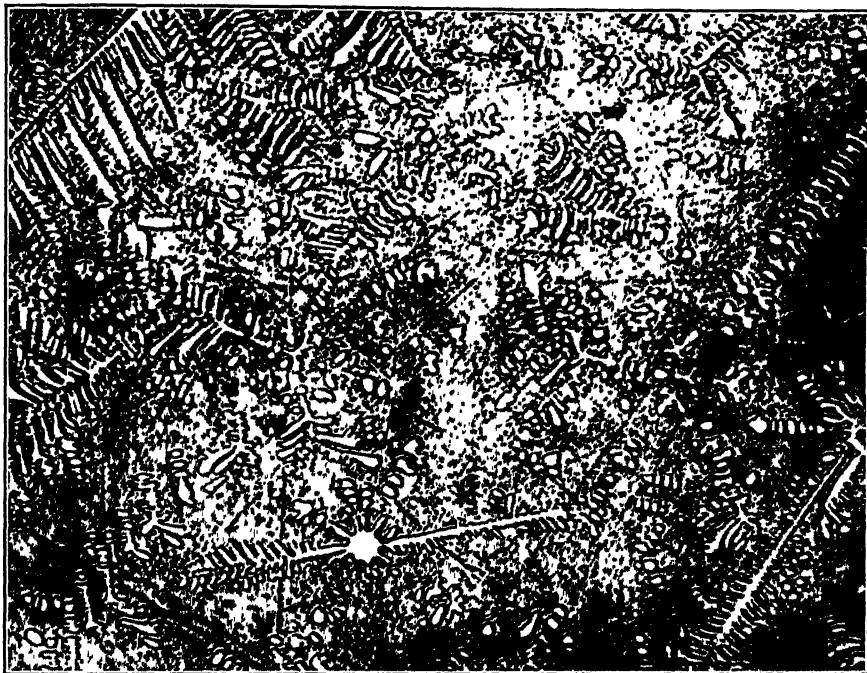


FIG. 9.—PORTION OF SAME FIELD SHOWN IN FIG. 4, UNDER AXIAL ILLUMINATION.

desired to study this, the proper objective and eyepiece to give the desired magnification should be determined and then with the arc condenser iris almost wide open, introduce a  $\frac{1}{2}$  or  $\frac{3}{4}$  in. diameter disk into the light beam between the iris and the light filter, as described. The shadow of the disk on the filter will assist in the manipulation. A good plan is to eclipse the light beam by slowly passing the disk through it, first vertically and then horizontally. Fig. 10 shows the light beam on the filter in eight positions as follows: Position 1, ordinary appearance, axial illumination; position 2, eclipse commencing, disk passing from top to bottom, no apparent effect optically; position 3, eclipse a little more than half complete, oblique light beginning to predominate from one direction and relief manifested in microconstituents; position 4,

eclipse almost complete and light becoming more oblique; position 5, eclipse has been completed and a few oblique rays are again illuminating the specimen but from the opposite direction; position 6, same as position 3; position 7, equivalent to position 2, axial rays again coming into play and masking relief effect; position 8, passage complete. This procedure may be repeated with a horizontal movement of the disk, or along a diagonal.

After finding the proper size of iris opening, size of disk, and degree of eccentricity, it is a good plan to rotate the disk about the optic axis and to note the effect of thus changing the direction of lighting. The wide-open iris and  $\frac{3}{4}$ -in. disk will meet most requirements, but some conditions

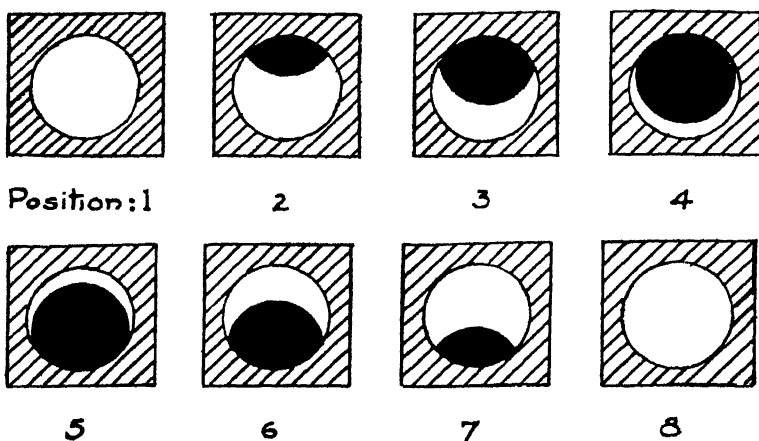


FIG. 10.—APPEARANCE OF LIGHT BEAM ON LIGHT FILTER AS DISK PASSES DOWNWARD ACROSS THE ILLUMINATING BEAM.

may demand a little experimenting with various combinations of openings and disks and it often takes some patience to determine a satisfactory combination and position. Practice brings familiarity and facility, as it does with the mechanical stage and focusing.

It will be found useful to adopt some scheme of reference so that any given combination of iris opening, stop diameter, and position can be duplicated. One method is to note the angular position of the disk shadow on the filter and refer to it as at 12 o'clock, 3 o'clock, 9 o'clock, etc. The disk size can be referred to by number, the number designating the disk diameter in eighths of an inch. The extent to which the disk eclipses the beam need not be referred to, although it would perhaps be desirable to do so; but as there is usually a best position of disk, that is, degree of eclipse, this position may be readily duplicated.

The need for knowing the direction at which light strikes the object has been referred to. A knowledge of the relationship between position of disk and direction of lighting is indispensable for intelligent work.

Without this information, it is impossible to tell, in the case of an unknown structure, whether the appearance is real or an illusion. An easy way of determining the direction of light is to select a field having two polishing scratches, which cross each other at right angles, and with their aid to note the direction of the light with the disk in several positions.

I POSITION OF SHADOW OF DISC ON LIGHT FILTER	II. DIRECTION OF LIGHT ON FIELD AS SEEN	
	ON GROUND GLASS	AT EYEPIECE (HORIZ POSITION)

FIG. 11.—DIRECTION OF LIGHT AT EYEPIECE AND AT GROUND GLASS FOR VARIOUS POSITIONS OF THE DISK.

The use of polishing scratches in this connection was illustrated in the previous paper. A simpler method is to push the disk somewhat nearer the center of the light beam than would ordinarily be done and thus cast a shadow on the field; the direction of light is then easily noted.

This relationship for the Bausch & Lomb, inverted-type microscope used by the writer is shown in Fig. 11. Column 1 shows the position of



FIG. 12.—IRON-CHROMIUM-CARBON ALLOY CASTING (AT SURFACE) UNDER CONICAL ILLUMINATION; ETCHED.  $\times 2000$ .

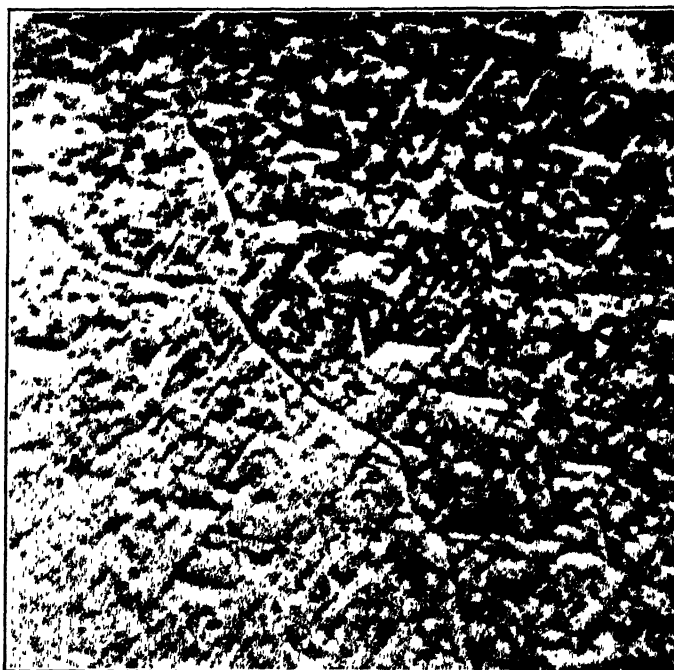


FIG. 13.—SAME MATERIAL AND MAGNIFICATION AS IN FIG. 12 BUT 0.02 IN. BELOW SURFACE OF CASTING.

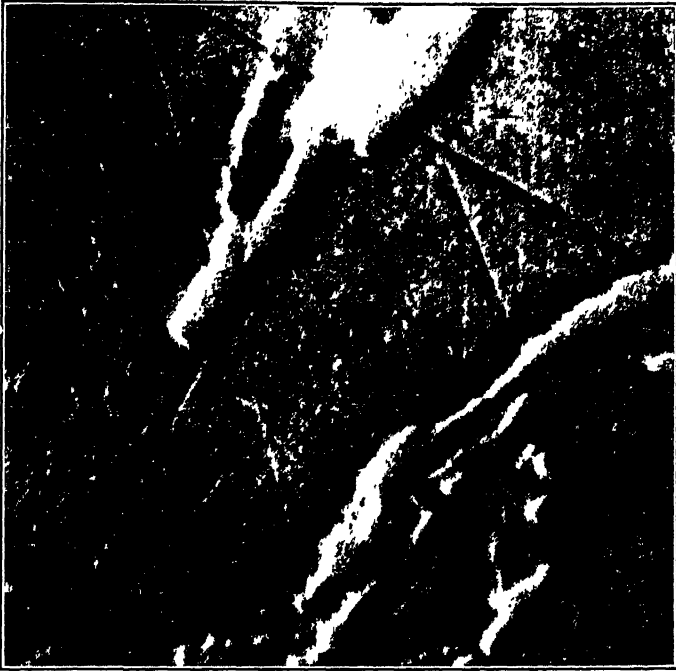


FIG. 14.—SAME AS FIG. 12, EXCEPT 0.04 IN. BELOW SURFACE OF CASTING; NOTE USE OF POLISHING SCRATCHES TO INDICATE MINERALOGICAL HARDNESS.



FIG. 15.—SIMILAR STRUCTURE TO THAT SHOWN IN FIG. 14, ALSO UNDER CONICAL ILLUMINATION, BUT AT 1000 DIAMETERS.

the stop diagrammatically; column 2 indicates the direction in which light comes to the field, as seen on the ground glass (incidentally, this is the same for the negative or print if they are orientated correctly); column 3 gives the same information with respect to the view as seen through the eyepiece.

It has been shown that simulation of natural lighting by means of conical illumination admits of more accurate interpretation. Moreover, as the following example will demonstrate, axial illumination may fail to reveal the presence of a constituent that is made clearly visible by the new method. An instance of this was afforded during an examina-



FIG. 16.—SAME FIELD AND MAGNIFICATION AS IN FIG. 15, BUT TAKEN WITH AXIAL ILLUMINATION, WHICH OBLITERATES ONE OF THE CONSTITUENTS.

tion of an iron-chromium alloy, containing 25 per cent. of chromium and 1 per cent. of carbon, in the cast condition. The polished surface was etched with cold Murakami's reagent, which gave the carbides in the body of the casting a greenish tint but left uncolored the higher carbides situated close to the surface.

Conical illumination was used to study the structure close to the surface, which corresponded to a chill, and to trace the gradual diminution in hardness from the surface inward by means of the polishing scratches. These were entirely absent at the surface and increased in number and magnitude toward the center. This transition is shown in Figs. 12, 13, and 14. Fig. 12 shows the higher carbide at the surface; no scratches are visible. Fig. 13 shows the structure 0.02 in. below the surface with one or two scratches traversing an octahedral structure. Fig. 14 is typical of the main body of the casting below 0.04 in. from the surface. The carbides, shown in relief, are of a different character than

those on the surface and were originally colored, but this coloring was subsequently rubbed off. The relief shown is partly due to polishing and partly to etching. It will be noticed that the polishing scratches in Fig. 14 are numerous; they do not, however, touch the hard carbide.

Figs. 14 and 15 reveal the feature that is invisible under axial light; Fig. 15 shows the same structure, though not the same field as Fig. 14, after longer etching. The greenish tinge was not rubbed off and consequently the colored carbide photographs dark. Associated with this colored carbide is an uncolored constituent, probably a carbide; it is barely discernible in Fig. 14 on account of the shorter etch. It was noticed that polishing scratches frequently cut the uncolored carbide but never the colored harder carbide. The fact that some scratches were interrupted by the uncolored carbide indicate it to be somewhat harder than the matrix but softer than the colored constituent. Fig. 16 shows the same field as Fig. 15 but under axial illumination. The uncolored constituent, which is brought out by conical illumination in Fig. 15, is rendered invisible in Fig. 16 by the masking effect of axial light.

High magnification was used in the foregoing example for the purpose of studying polishing scratches with relation to structure, and not structure alone, for the latter can be easily seen under lower magnification. This example was chosen to illustrate the application of conical illumination to metallography, particularly the utilization of polishing scratches for the interpretation of physical properties of microconstituents and to furnish a specific instance of increased revelation made possible by conical illumination.



## Overstrain in Metals

BY JOSEPH KAYE WOOD, NEW YORK, N. Y.

(New York Meeting, February, 1924)

A METAL is said to be overstrained when it is deformed beyond the elastic limit at a temperature well below the critical range, as in cold working. Quantitatively, overstrain might be considered as that part of the total elastic deformation of the piece of metal, left over after the external load is removed, that added to the permanent deformation due to plastic action will give the total permanent deformation. Ordinarily the effects of this phenomenon, which vary with the internal residual stress probably in accordance with Hooke's law, are more noticeable when the yield point of the metal is exceeded, but they probably also exist to a smaller degree when the load is just large enough to cause the least amount of permanent set. These effects, which we recognize as the result of overstrain, are as follows:

1. An apparent increase of the elastic limit in tension and a decrease of the elastic limit in compression, provided the external load is tensile. The reverse is true when the load is compressive.

2. An elastic after-effect in which time and temperature are important factors.

3. A state of imperfect elasticity in which Hooke's straight line becomes slightly curved, giving rise to an hysteresis loop.

4. In addition to the apparent increase in the elastic limit, such properties as the hardness, ultimate strength, and resistance to fatigue failure are increased, provided the overstraining has not been carried far enough to make the metal brittle.

5. Correspondingly the ultimate elongation, reduction in area, magnetic quality, ratio of endurance limit (fatigue breaking stress) to elastic limit, and resistance to season cracking (in certain copper alloys) are decreased.

The question naturally arises: how do these changes in the properties of a metal resulting from overstrain influence our method of design? The fact that most of the desirable qualities are increased makes overstraining a favorable process, from an engineering standpoint; but on the other hand, the loss of such qualities as perfect elasticity and complete

elastic recovery (absence of elastic after-effect) may be a serious defect in certain cases. For example, spiral and helical springs used in delicate measuring instruments should not show any elastic after-effect, because it is required that the indicating needle shall be returned automatically to the zero reading, immediately after the impulse being measured is released. Another example is that of flat electrical contact springs which, after being assembled in "pileups" of two or more springs, are usually adjusted by bending (overstraining) them just enough to obtain the proper air gap between the contacts attached to the free ends. This adjustment may change gradually in a few weeks or months, depending on the kind of metal used, because of elastic after-effect. The elastic hysteresis effect, as pointed out by F. J. Schlink,<sup>1</sup> is analogous to mechanical backlash; and although it is negligible in ordinary cases, it is quite appreciable in the case of measuring instruments. Brass parts, in particular, are subject to season cracking when overstrained; while the magnetic quality of iron or steel is decreased.

#### DEFORMATION OF A SINGLE CRYSTAL GRAIN

The quantities obtained when testing a tensile specimen are largely statistical in character, because of the different orientations of the crystallographic planes and the dispersion of hard among soft crystalline grains. This fact may be better understood by considering what takes place within the space lattice of a single crystal grain when loading and unloading the specimen and also developing the stress-strain diagram.

The irregular polygonal shapes seen when an etched specimen is placed under the microscope will be referred to simply as "grains" while the fundamental unit of space lattice structure within these grains will be termed the "lattice unit." It is conceded by many authorities that a grain is deformed elastically up to the point where slipping along the crystallographic planes takes place. The grain is then said to yield plastically up to the breaking point, the slipping distance being called the permanent set. Fig. 2 shows the stress-strain diagram for the condition of loading shown in Fig. 1, which in (a) shows a single grain as a simple cube with the crystallographic or easy slip planes marked in dotted lines, while (b) shows this grain deformed elastically by the shearing couple  $E$ . The corresponding deformation 4 is shown plotted in Fig. 2. Plastic deformation seemingly obeys the law of the viscous flow of liquids, namely that the rate of deformation is directly proportional to the pressure. Consequently if just a small increment of load beyond  $E$  causes slip along the weakest slip plane, as shown in Fig. 1 (c), the curve in Fig. 2 would continue as a horizontal line from the point 1. This theoretical

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<sup>1</sup> The Study of Mechanical Hysteresis. *Eng. News-Record* (1918) 80, 1035.

stress-strain diagram would also represent the artificial structure shown in Fig. 3 under a similar condition of loading, in which a number of the same kind of granular cubes are placed together in such a way that the slip planes are continuous. We thus have two areas under the curve;

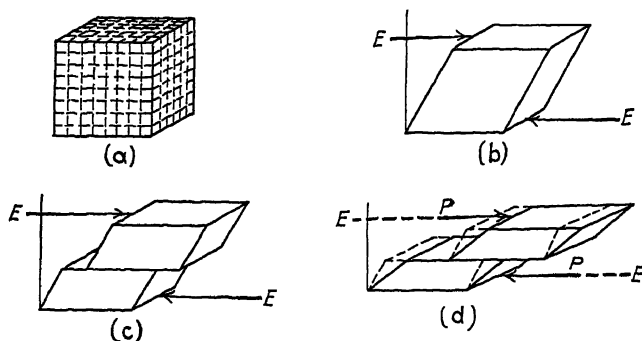


FIG. 1.—ELASTIC AND PLASTIC DEFORMATION OF AN IDEAL CRYSTALLINE GRAIN, GREATLY EXAGGERATED.

area 1-4-5 representing the elastic energy and area 1-2-3-4 the plastic flow energy, the sum of the two 1-2-3-4-5 representing the total resistance offered by the grain. This resistance is therefore the toughness of the grain; and although a certain grain may have a higher elastic limit and

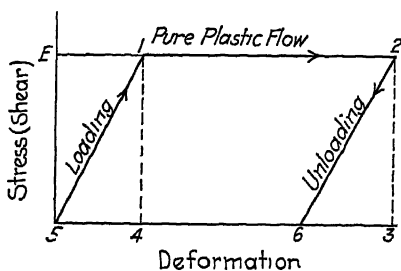


FIG. 2.—IDEAL STRESS-STRAIN DIAGRAM FOR THE DEFORMATION OF A SINGLE CRYSTALLINE GRAIN UP TO THE YIELD POINT.

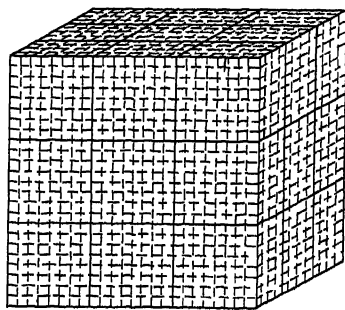


FIG. 3.—IDEAL ARRANGEMENT IN THEORETICAL AGGREGATE OF CRYSTALLINE GRAINS.

breaking strength than another grain it may not be as tough because of a much smaller plastic flow resistance. Line 2-6 shows the unloading of the grain and as it is, in general, parallel to line 1-5 we may consider the elastic energy 100 per cent. resilient, the areas 2-3-6 and 1-4-5 being equal.

Now, suppose instead of stopping at just a small increment above the load  $E$  we continue to, say, load  $P$ , Fig. 4. The blocklets of the cube on either side of the slip plane will continue to deform elastically, provided slip does not occur along other slip planes. Even if slip has occurred along several slip planes, which is more likely to occur in an actual aggregate of grains, the individual blocklets will be deformed elastically and the sum total of these deformations will be the same as if no slip had occurred on any of the planes. With increase of load above  $E$ , the elastic deformations take place simultaneously with the plastic deformations. Assuming a uniform rate of loading, the rate of plastic flow will not be constant along the line 1-2, as in Fig. 2, but will be uniformly accelerated because of the elastic transmission of the uniformly increasing loads

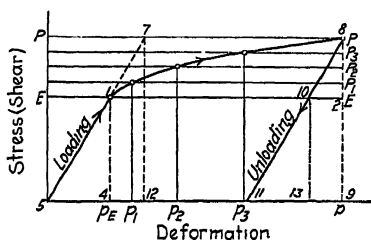


FIG. 4.—IDEAL STRESS-STRAIN DIAGRAM FOR THE DEFORMATION OF A SINGLE CRYSTALLINE GRAIN BEYOND THE YIELD POINT.

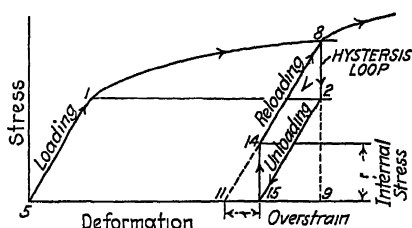


FIG. 5.—STRESS-STRAIN DIAGRAM FOR THE DEFORMATION OF AN AGGREGATE OF CRYSTALLINE GRAINS—OVER-STRAIN.

through the blocklets. Fig. 1 (*d*) shows a grain deformed in this manner, the full lines corresponding to the load  $E$  and the dotted lines to the load  $P$ . Of course when the load  $P$  is once reached and kept constant, the rate of plastic flow will also be constant, as was the case for the constant load  $E$ , but it will be greater than the rate for the latter load. To simplify the discussion, the stress-strain diagram is redrawn as shown in Fig. 4, in which 5-1-2, is the same as shown in Fig. 2. The fact that the amount of elastic deformation in the grain is the same whether slip takes place or not, permits us to extend the elastic line from  $E$  to  $P$  temporarily, as shown by the dotted line 1-7. The lines drawn parallel to 1-2 divide the load increment  $E-P$  into four equal parts which, because of the uniform rate of loading, also divide the corresponding time interval into four equal parts. As a result of the accelerated plastic flow, the deformations corresponding to the equal time intervals grow larger and larger; that is,  $p_E$  will be the deformation corresponding to load  $E$  at the beginning of plastic flow,  $p_1$  that corresponding to the load  $P_1$ ,  $p_2$  to the load  $P_2$ ,  $p_3$  to the load  $P_3$ , and  $p$  to the load  $P$ . Where the verticals erected at these deformations intersect their respective load lines, determine the continuation of the stress-strain diagram from the point 1. Thus is obtained the

fundamental shape of the stress-strain diagram based on a single grain and in it the general shape of the curves determined by actual tests can be recognized.

Releasing all load results in 100 per cent. recovery of the elastic energy, that is, the unloading line 8-11 will be parallel to 7-1-5. The total elastic energy returned is represented by area 8-9-11 while the plastic energy not returned is 1-8-10-11-5. If the load causing plastic flow had been constant at  $P$ , instead of varying from  $E$  to  $P$ , the plastic energy would have been represented by the square area 7-8-9-12.

### DEFORMATION OF AGGREGATE OF CRYSTAL GRAINS

In the case of a pure metal in the vapor state, the atoms or groups of atoms (molecules) that would be relatively far apart move at random with great velocity because of heat energy. Abstracting a large amount of this kinetic energy results in the liquid state, with which we are familiar, and in which the molecules have a strong tendency to group into minute chains. This is due to the intense electromagnetic fields surrounding atoms, although the force of these fields is slightly overbalanced by the remaining thermal forces. Further abstraction of heat energy decreases the amplitude of the thermic vibrations sufficiently to permit the electromagnetic forces to hold the atoms rigidly in place. Thus the atoms are arranged in a definite manner, depending on the metallic element involved, which gives rise to the space lattice or crystalline type of construction. The character of the electromagnetic forces for the various metallic elements is such that the cubic space lattice, either face or body centered, is formed; an arrangement which probably starts with the formation of the chains just mentioned, arms growing outwards  $90^\circ$  therefrom until, in the solid state, we have the well-known dendritic, or pine tree, formation. The dendrites keep on growing until they interfere with one another, giving rise to crystal grains that, in metals, may attain a size of 0.001 in. It is these grains we are about to consider in aggregation. Because of the natural randomness with which the molecular chains in the liquid state discard themselves, we would expect the orientations of the dendrites, and consequently the crystallographic planes of the lattice structure within different dendritic grains, to be likewise variable. In the process of solidification, some of the atoms are not favorably disposed to take their positions in the lattice structure within the grains and consequently are secured rigidly between them. This irregular disposition of atoms in the solid or amorphous state is, at the most, only a very thin film entirely surrounding each grain. As this amorphous state obeys the law of viscous flow, it is often referred to as an undercooled liquid of high viscosity. This and other facts led to the belief that the phenomenon of plastic flow is due to the formation of

amorphous metal along the slip planes, particularly as in a metallic aggregate the slip on each plane is limited, the total slip being the result of the summation of movements on many slip planes. The amorphous metal is supposed to be produced by the tearing of atoms from the space lattice at the beginning of slip, which causes considerable localized heat to be generated. Dissipation of this heat decreases the mobility of the amorphous layer and prevents further slipping; the metal, as a whole, is made harder because slip cannot take place in a random mass of atoms as readily as in space lattice. Ingenious as this amorphous-cement theory may seem it is not accepted by certain schools, but the writer does not feel inclined to take part in the discussion and will suggest another explanation later. The point in dispute does not include the amorphous film around the crystal grains, but only that which is supposed to be formed on the slip planes.

Assume then that an aggregate of crystal grains is oriented in all possible ways and that each is surrounded by a very thin amorphous film; also that we are dealing with a pure metal in a normalized condition. According to Fig. 3, in order to break the continuity of the crystallographic or easy slip planes, the grains can be rotated only through angles less than  $90^\circ$  about each principal axis. Thus, in an actual aggregate of grains, the variation in the orientations of these planes is limited, so that when tension is applied to a tensile specimen, most of the grains are subject to a shearing couple, as in Fig. 1, and possibly a componental tension acting normal to shear. Direct tension alone probably does not occur to such an extent, as there is only one possible position of the grain within each of the  $90^\circ$  variations that will give this condition. For the grain position making  $45^\circ$  with the axis of the specimen, the shearing couple is a maximum.

It is doubtful whether tension on single grains exists to a large extent, because the loading would have to be uniform over the entire surface of a grain to prevent slipping on easy slip planes, which monochromatic light shows to be only about 0.00002 in. apart<sup>2</sup> while x-rays show that the distance between two adjacent crystallographic planes is in the order of  $12 \times 10^{-9}$  in. for metallic elements. Jeffries and Archer<sup>3</sup> describe the behavior of a single grain under tension (Fig. 1) and point out that the componental tensions must become shearing forces after slip has subsided on the planes normal to them.

The total elongation, therefore, in the specimen we are considering is equal to the total effect of the deformations (both elastic and plastic) of each grain multiplied by the cosine of the angle that grain makes with the axis of the specimen. As loading is applied all deformations will be

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<sup>2</sup> Rosenhain's "Introduction to Physical Metallurgy."

<sup>3</sup> The Slip Interference Theory of the Hardening of Metals. *Chem. & Met. Eng.* (1921) 24, 1057.

elastic until those with short projections on the axis begin to yield plastically. The plastic deformations begin in the order of the increasing projected lengths and during this plastic flow the resulting blocklets simultaneously continue to be loaded elastically, but with inappreciable deformations because of the additional stiffening obtained from the amorphous layers around the deformed grains and interference with adjacent grains. The grains having small projections tend to interfere with the slip of grains having larger projections, which is in accordance with Jeffries and Archer's theory of the hardening of metals. This interference is increased with a decrease in grain size and in mixed aggregates of soft and hard grains. The amorphous layers give added stiffness because the periphery of a grain deformed plastically is increased; while it is hardly changed for an elastically deformed grain, which fact must account somewhat for the many slip planes formed in a single grain in an aggregate.

Reference to Fig. 4 will show that the stress-strain diagram for the deformation of a single grain may be divided into two principal areas, the elastic energy area 5-1-7-12 and the plastic energy area 4-1-8-10-13. The elastic area may be subdivided into two other areas, which may be called the hypoelastic area 5-1-4, occurring up to the elastic limit,<sup>4</sup> and the hyperelastic area 4-1-7-12, occurring beyond the elastic limit. From these considerations a similar curve holds for an aggregate of grains, except that hyperelastic energy (1) is greater because of the earlier occurrence of plastic action and continued elastic action, and (2) is stored within the specimen because of internal interference giving rise to internal stresses. Thus, in Fig. 5, the unloading line is not 8-11, representing full recovery of the hyperelastic energy, as for the single grain, but is 8-2-15, which shows that all of this energy is stored within the material. That is, in releasing the load from 8 to 2 practically no deformation takes place in the reverse direction because the resistance offered by the adjacent grains and amorphous layers to those grains tending to be deformed hyperelastically (grains in which slip has already occurred) is being relieved. At point 2, this resistance is reduced to zero and the unloading is completed along the hypo-, or pure, elastic line. The grains which were free to extend hypoelastically, that is, those grains in which no slipping took place during the total deformation 5-9 of the specimen and which met with little or no interference, require a greater back deformation than 9-11 to relieve them entirely of stress, as indicated by the slope of the line 1-5. Thus, the specimen will have an internal stress 15-14, corresponding to the deficiency 15-11 in back deformation, that, when the specimen is reloaded, will have to be overcome before any direct deformation takes place. This deficiency in

<sup>4</sup> Elastic limit is being used throughout this paper as synonymous with the proportional limit.

deformation that is left over may be termed "overstrain." From the point 14, the stress-strain diagram is exactly the same as the original loading and each succeeding loading is the same except that the internal stress is increased over the preceding one. Fig. 6 shows the first three consecutive loadings and unloadings of a specimen after it has been normalized. The introduction of an increasing internal stress with a cor-

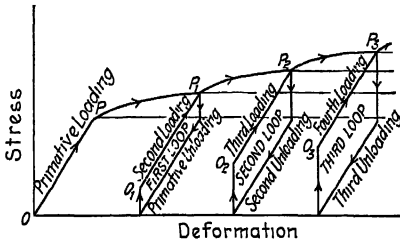


FIG. 6.—PROGRESSIVE INCREASE IN ELASTIC LIMIT (APPARENT) AND AREA OF LOOPS RESULTING FROM PROGRESSIVE OVERSTRAIN.

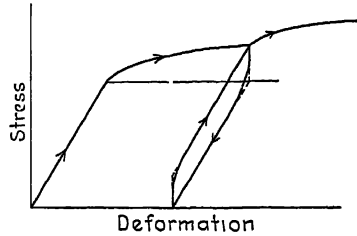


FIG. 7.—MORE EXACT SHAPE OF HYSTERESIS LOOP.

respondingly increasing overstrain raises the zero point of the fundamental stress-strain diagram (first loading line), which results in a raising of the fundamental elastic limit  $P$  to the apparent elastic limits  $P_1$  and  $P_2$ . The area of the hysteresis loop, which is equal to the hyper- or stored energy area minus the overstrain energy area, is also increased with each reloading, in consequence of which the tensile strength, fatigue quality, and hardness are increased. The corresponding properties, such as the ultimate elongation, reduction in area, etc., are decreased.

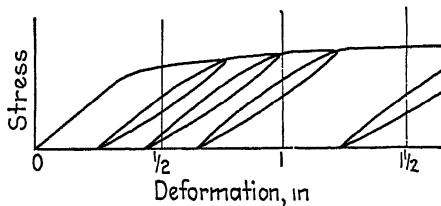


FIG. 8.—ACTUAL STRESS DIAGRAM FOR BRASS OBTAINED BY PROFESSOR DALBY.

Inasmuch as the foregoing effects are statistical in character, we should not expect to find in an actual test a sharp change in direction in going from the line representing the internal tension to the line of elastic deformation. Instead, we should expect the hysteresis loop to have curved lines, as shown by the full lines in Fig. 7. This expectation is fulfilled by the curve shown in Fig. 8, which represents an actual test on a specimen of brass performed by Professor Dalby with the aid of his optical load extension recorder attached to a tensile testing machine. This curve shows that repeated overstraining raises the apparent elastic



limit and increases the area of the hysteresis loop. As in the theoretical diagram, Fig. 7, it also shows imperfect elasticity for all loadings except the first. Inasmuch as no interference takes place in deforming a single grain, we would not expect to experience overstrain or elastic after-effect in this case. Tammann found this to be so in testing his small tungsten wires of single grain diameter.

At point 2, Fig. 9, the internal tension corresponding to overstrain exists in the hypoelastic grains, but in order to maintain equilibrium, the hyperelastic grains (those in which slip has occurred) must be in compression. Thus when a reversed loading, *i.e.*, compression, is placed on the specimen the elastic limit in compression will be reached much sooner

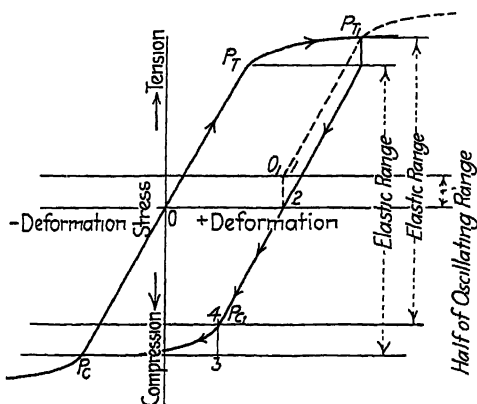


FIG. 9.—EFFECT OF OVERSTRAIN ON ELASTIC LIMIT IN COMPRESSION; ELASTIC RANGE REMAINS CONSTANT BUT OSCILLATES.

than when the specimen is originally loaded in compression, as shown by the line  $0-P_C$ . Assuming the elastic limits  $P_C$  and  $P_T$  to be equal,<sup>5</sup> for the sake of simplicity, although the same results are obtained for unequal limits, we can readily ascertain the effect of a smaller limit in compression. Laying off the initial compressive stress, equal to 1-2 the internal tension, from the  $P_C$  line toward the zero axis a distance (3-4) we obtain the new limit  $P_{C1}$  in compression. Exceeding this new limit introduces an overstrain in compression which, when the specimen is loaded in tension, again causes the elastic limit in tension to be lowered. In other words, the hypoelastic range  $P_C-P_T$  remains constant for reversed tensile and compressive loadings, but because of the hyperelastic energy this range oscillates as a whole either side of the zero axis. It is this oscillation that causes fatigue failure in the hyperelastic grains, being produced by the continual slipping of the blocklets back and forth within these grains. For

<sup>5</sup> These correspond to Baushinger's primitive elastic limits while the raised or lowered limits  $P_{T1}$  or  $P_{C1}$  correspond to his natural elastic limits.

stresses within this true range, we should have no oscillation and consequently no fatigue failure. For stresses outside of this range, fatigue failure may be delayed somewhat by the annealing effect of the running temperature on overstrain.

#### ELASTIC AFTER-EFFECT

Elastic after-effect, which is the loss of overstrain after unloading is completed, depends chiefly on the factors of time and temperature. Our previous study showed that overstrain is caused by the hyper-, or stored, elastic energy, resulting from the interference offered by the hypo-elastic grains. The hyperelastic grains are in compression at the moment the external tension is removed. Hence if this compressive stress is smaller than a critical pressure, corresponding to the shear  $E$ , Fig. 2, no plastic flow will occur and no elastic after-effect, or back-deformation

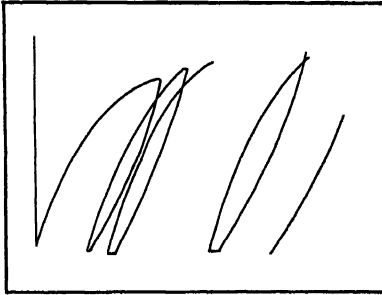


FIG. 10.—ELASTIC AFTER-EFFECT IN ZINC, ACCORDING TO DALBY.

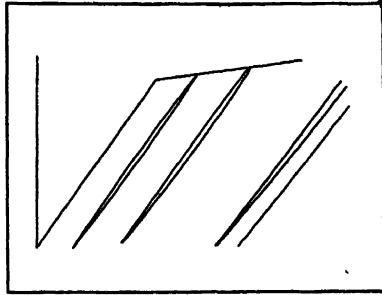


FIG. 11.—OVERSTRAIN IN STEEL, ACCORDING TO DALBY.

from 15-11, Fig. 5, will take place. If the compressive stress is just equal to the shear  $E$ , elastic after-effect takes place slowly, requiring anywhere from a few minutes to several months (aging) for the full back-deformation 15-11 to be completed. If the stress is larger than  $E$ , elastic after-effect will not take place within reasonable lengths of time. However, the application of heat in the form of boiling water, or low-temperature annealing, will reduce  $E$  so that elastic after-effect will be greatly hastened or made possible. Inasmuch as the value of  $E$  varies considerably at room temperature for the different metals, we would expect the elastic after-effect to be variable for a given internal compression of the hyper-elastic grains. This effect takes place in zinc almost immediately after the unloading of the specimen, as shown by Fig. 10, which represents a test made by Professor Dalby. Soft iron shows the effect only when boiled in water (212° F.) while it requires more elevated temperatures (around 600° F.) for certain steels and phosphor-bronzes. Fig. 11 shows that the effect does not take place in steel at ordinary temperature immediately after unloading.

This releasing of overstrain, by causing plastic flow in the hyper-elastic grains with the implements of time and temperature, may be described as the acceleration of elastic after-effect by aging and low-temperature annealing. With these phenomena, all effects due to overstrain

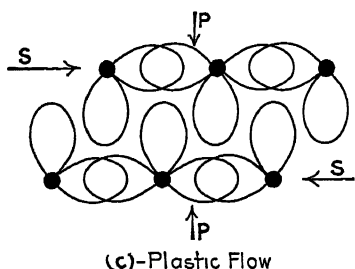
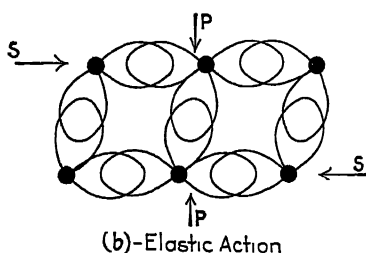
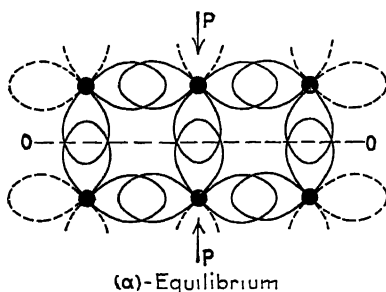


FIG. 12.—ATOMIC ACTION IN DEFORMATION.

disappear and the material reverts to the normalized state, which is represented by the fundamental stress-strain diagram, showing the primitive elastic limits. We therefore have a means of eliminating elastic after-effect in helical and spiral springs used in instruments, of eliminating the tendency in brass to season crack, and of restoring perfect elasticity. Spring adjustments would be insured by a temperature process which would eliminate gradual creepage.

#### ATOMIC ACTION IN ELASTIC AND PLASTIC DEFORMATION<sup>6</sup>

A simple arrangement of atoms (black dots) taken from a cubic space lattice to which most of the metals conform is shown at (a) Fig. 12. The loops emanating from the atoms represent the closed electromagnetic circuits, which hold the atoms in the space lattice against the tendency of the thermic vibrations, which are much reduced in the solid state. The arrowheads show that the direction of the forces tends to produce a powerful pressure  $P$ , acting normal to the shearing couple  $S$ . To

cause a break, along the plane 0-0, by opposing the normal  $P$  would require breaking all the atomic bonds simultaneously; while for a shearing couple  $E$  the bonds are broken progressively, as shown in (b) and (c). The first represents elastic deformation, which shows only a slight rotation of the electromagnetic fields, while the second shows an actual breaking of the atomic bonds. With the breaking of the atomic bonds on this slip plane, the thermic vibrations are free to act (condition of liquid phase) which probably accounts for the viscous behavior in plastic deformation. When the plastic flow on the slip plane is completed, as in (a), the atomic

<sup>6</sup>Probable explanation of the phenomenon of plastic flow referred to in the first paragraph of page 6.

bonds are once more established, which corresponds to the apparent sudden hardness referred to in the amorphous-cement theory. At this stage the atomic bonds in the weakest of the remaining slip planes are broken, whereupon plastic flow takes place and the atomic bonds are again reestablished as before. This process is repeated many times within a single grain, particularly in an aggregate of grains where interference to slip is considerable as pointed out previously. This process of reasoning, confirmed by suitable tests, might serve as a basis for a theory that would account for many of the phenomena occurring in metals, as in the following instances:

1. In releasing internal stress by heat, the thermic vibrations are increased in amplitude, which decreases the viscosity of the liquid phase on the slip planes of the hyperelastic grains. The internal compression therefore, having less resistance to overcome, causes a back-deformation.

2. It has been shown<sup>7</sup> that elastic deformation affects the intensity of magnetization while permanent deformation does not. Fig. 12 (b) and (c) show the reason for this. In the former there is a rotation of the atoms against the electromagnetic forces that should tend to constrain the complete alignment of the elementary magnets giving the maximum, or total intensity, of magnetization; while in the latter there is no such rotation, hence no constraint against the complete alignment of the elementary magnets.

3. The relative brittleness and ductility of the various metals depend chiefly on the value of the normal  $P$ , which pressure is an inherent property of the metal depending, as it does, on the electromagnetic forces of the atoms. In brittle metals, the atomic bond is broken with the least amount of distortion, although the relative stiffness may be high, mainly because  $P$  is small, while in ductile metals the bond is maintained mainly because  $P$  is large. Hence, brittle metals could probably be made ductile if  $P$  could be increased artificially,<sup>8</sup> or ductile metals made brittle if  $P$  could be decreased.

4. The characteristic brittle break of a ductile metal, when subject to impact, may also be explained. Suppose that a cast-iron vessel is filled with a liquid corresponding to the plastic phase and that there is an orifice in the lower end of the vessel and a liquid-tight piston at the top. If the piston is subjected to an impact, the liquid can flow through the orifice only at a definite rate, depending on its viscosity, consequently the great amount of impact energy occurring in a small interval of time will be transmitted to the walls of the vessels, wherein a stress sufficient to fracture the vessel may be built up. A similar action occurs in a metal

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<sup>7</sup> L. Fraichet: Magnetization and Molecular Deformation of Steel under Tension-elastic Limit. *Rev. de Metall.* (Jan., 1923).

<sup>8</sup> A. A. Griffith: The Phenomena of Rupture and Flow in Solids. *Phil. Trans. Royal Society of London*, 221, 187.

under impact. The strength of the brittle vessel corresponds to the normal  $P$  in Fig. 12(b) and the liquid to the plastic phase during slip. When impact in shear  $S$  is applied, the rate of flow or slipping is a definite amount like the flow of liquid through the orifice. Consequently, the energy of impact reacts against the "walls" of the blocklets (line 0-0), where it acts against the normal  $P$  thereby breaking all the atomic bonds and resulting in a characteristic brittle break.

## Nitrogen in Steel

Discussion of the paper by C. BALDWIN SAWYER, presented at the Canadian Meeting, August, 1923, and printed in Vol. LXIX, p. 798.

J. S. VANICK,\* Washington, D. C. (written discussion).—To those who have been confronted with the study of the gas-metal reactions, this paper is a most welcome contribution. My personal interest in work bearing upon this general problem, stimulated by an appreciation of the difficulties inherent to problems of this type, prompts a few words of discussion.

Table 2 of the paper shows a gradual increase in the nitrogen content with an increase in pressure, and an interpretation follows in which nitrogen is used as the compressed medium when the conditions admit that cyanogen gas could be active as a contaminating ingredient. Fusions of electrolytic iron made in the induction furnace in an atmosphere of deoxidized nitrogen and out of contact with contaminating materials have shown no microscopic evidence of a nitrogen increase; using a refractory-lined graphite crucible in the furnace under the same conditions or admitting air often resulted in the occurrence of nitride needles in the solidified melt. These results suggested that a nitrogenous compound served as a vehicle for the introduction of nitrogen and that such compound was not available when the pure gas and carbon-free refractory were used. The fusion of pure iron in pure nitrogen is perhaps a matter of theoretical interest. The author's work serves a more practical purpose when applied to steels rather than iron.

Table 2 reports the absence of nitride needles in melts made under pressure of one atmosphere, although the quantity of nitrogen present would seem to exceed microscopically detectable percentages. In some recent work<sup>20</sup> on carburized iron, nitride needles have been observed in areas analyzing as low as 0.015 per cent. nitrogen. This low percentage of nitrogen would indicate that the solubility limit is less than 0.030 per cent. for hypoeutectoid steels. There is the possibility that the areas of pearlite which exist in a hypoeutectoid steel restrict the distribution of nitrogen and limit its presence to the ferritic fields. In view of this work and the references quoted by the author, I am led to expect that the value for the solubility of nitrogen in solidified iron may approach

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<sup>20</sup> *Trans. Am. Soc. for Steel Treating* (1923).

the 0.02 per cent. mentioned by Tschischewski, when conditions are favorable for its precipitation.



FIG. 27.—WHITE AND BLACK LAYERS OF NITRIDE IN A CROSS-SECTION OF WIRE THAT HAD BEEN AMMONIA-NITROGENIZED AT 650° C.  $\times 75$ . (MOUNTED IN SOLDER.)



FIG. 28 —TRANSITION ZONE FROM SURFACE TO CORE OF A SPECIMEN AMMONIA-NITROGENIZED AT 650° C.  $\times 100$ . (a) OUTER LAYER, POROUS, WHITE NITRIDE. (b) INNER LAYER, COMPACT WHITE NITRIDE. (c) *b* AND *d* INTERMEDIATE. (d) BLACK BAND, EUTECTOID. (e) HYPOEUTECTOID. (f) NITRIDE NEEDED INTERIOR.

The determination of the composition of the 1.7 per cent. nitrogen "eutectoid" is of very great importance in establishing the position and

identity of this compound in the tentative iron-nitrogen diagram. Experiments made at this laboratory located the range of composition of the "black band" in ammonia-nitrogenized specimens between 1.6 and 2.3 per cent. nitrogen. The method consisted of exposing fine wires to a current of ammonia at 550° C. and calculating the total nitrogen content determined from an analysis of the entire wire into the percentage of area occupied by the white layer. Repeating this procedure at 650° C., and correcting for the area and composition of the white layer, gave the range of values above. This method is obviously too coarse to closely confine the composition limits of the compound.



FIG. 29.—A PORTION OF FIG 28 MAGNIFIED.  $\times 500$ .

The certainty with which the "black band" in ammonia-nitrogenized specimens appeared upon cooling from above 650° C. strongly emphasized this eutectoid characteristic. However, the microstructure of the "black band," or pearlitic patch, if resolved, possessed the martensitic or the flat, sorbitic structure; never the structure common to eutectoids. In addition, the failure to produce a hypereutectoid zone in specimens coated with the nitride layer and subsequently heated out of contact with ammonia, militated against its acceptance as a eutectoid. Future work may overcome these difficulties and resolve the character of the eutectoid components. Figs. 28 and 29 illustrate typical intermediate forms of the iron nitride which appear in passing from the surface to the interior of an ammonia-nitrogenized rod.



## Physical Defects in Hollow Drill Steel\*

BY FRANCIS B. FOLEY,† CHAS. Y. CLAYTON,‡ AND MUIR L. FREY,§ ROLLA, MO.

(New York Meeting, February, 1924)

DURING the past year, we have investigated the cause of 88 per cent. of the failures by breakage near the bit end of some 1-in. hollow, hexagon, drill steel used in a metal mine. This breakage in the region of the bit end of the steel was peculiarly interesting because we have been led to believe that breakage is most prevalent at the shank end of drill steels near the place where the steel is gripped in the chuck of the machine. Records from the mine showed, also, that the breakage was much more frequent in the short lengths of large gage than in the longer steels; this is shown graphically in Fig. 1. Because the shorter lengths of steels are usually those that have been made from broken pieces of long steels or from steels that have worn down in service, rarely being made from new stock, those who are wont to suspect steel of tiring and crystallizing in its old age through fatigue are quite apt to see in this instance an argument in favor of their idea. As usual, a careful examination of these steels reveals defects of a character hardly to be overlooked in favor of such a cause.

The steel in question was rolled with a sand core and was of the usual drill steel composition: Carbon 0.85 per cent., manganese 0.60 per cent., silicon 0.25 per cent., phosphorus 0.02 per cent., and sulfur 0.02 per cent., with the exception that in some specimens there was vanadium, not exceeding 0.20 per cent.

The following lengths and gages were used:

LENGTH, FEET	GAGE, INCHES	LENGTH, FEET	GAGE, INCHES
Starter	2 $\frac{3}{8}$	7	1 $\frac{3}{4}$
3	2 $\frac{1}{4}$	8	1 $\frac{1}{4}$
4	2 $\frac{1}{8}$	9	1 $\frac{3}{8}$
5	2	10	1 $\frac{1}{8}$
6	1 $\frac{5}{8}$		

\* Published by permission of the Director of the Bureau of Mines.

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When preparing specimens for this investigation, 12 in. of the bit end of steels representing each of the gages, nine in all and all in the sharpened but unhardened condition, were halved longitudinally by sawing. The faces thus exposed of one-half of each of the steels were polished and etched to develop structural changes in the metal, as shown in Fig. 2.

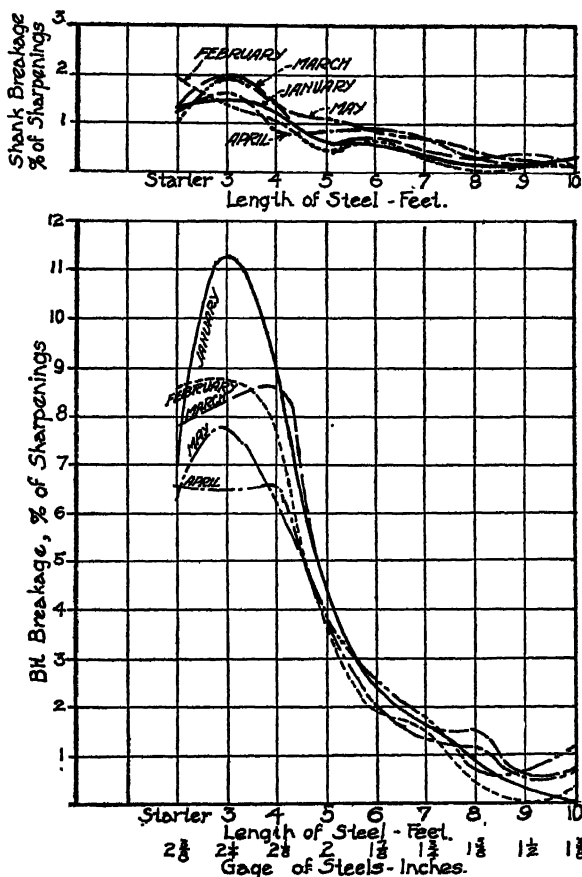


FIG. 1.—BREAKAGE, AS PERCENTAGE OF TOTAL SHARPENINGS FOR VARIOUS LENGTHS AND GAGES OF STEEL.

The lines bounding these zones of structural difference have been emphasized by tracing them with a pencil on the original pieces in order to bring them out more prominently in the photographs. The other halves were cut into convenient lengths, polished free of scratches for microscopic examination, and given careful scrutiny under a microscope for defects. The presence of quite a number of transverse cracks was thus revealed, the cracks usually extending from the water hole at right angles

into the metal. The depth and the angle that these cracks made with the water hole were recorded and their location, with reference to the length of steel, is shown in Table 1. The heavy line in each column



FIG. 2.—BITS NOS. 4, 5, 6, AND 7; MACRO-ETCH SEVEN-TENTHS ACTUAL SIZE.

indicates the position of the point of structural change farthest from the bit end, as revealed by the etching of one of the halves of each of the steels. This line, therefore, limits the region that was subjected to effective heating during sharpening and tempering.



Two cracks were found extending at right angles from the outside surface in bit No. 1, three in bit No. 2 (two of them in the upset portion), and five in bit No. 4. None of the other bits showed any cracks on the outside surface of the steel.

### DISCUSSION OF RESULTS

A study of the results for the purpose of establishing a relation, if any should exist, between the regions of structural change and the location and depth of the cracks found, reveals the following:

In bit No. 1, there are numerous crack areas a considerable distance outside the heated portion but the deepest cracks occur in the latter region. A group of cracks within the region of structural change contains two of the deepest, one of which is 1.848 and the other 1.344 mm. deep; both of these can be seen easily with the unaided eye.

In bit No. 2, there is apparently little relation between the cracks and the portion heated in the sharpening operations. This may be considered a relatively good piece of drill steel.

Bit No. 3 is similar to No. 2 in that it has few cracks and may be considered relatively sound; such unsoundness as exists is in the region of structural change.

In bit No. 4 is found once more the semblance of a relation between the area of most cracks and the portion subjected to heating; however, the deepest cracks occur just outside the region of structural change.

In bit No. 5, the worst condition with respect to cracks is in the region of structural change. There are five zones embracing areas in which there are numerous cracks, and four of these five zones are in that region. Practically all of the deepest cracks also are in this region. The bit is relatively in very poor condition; it may be cited as the poorest of the lot.

Bit No. 6 is poor but not as poor as No. 5; here, too, the region of deepest and most numerous cracks coincides with the region of structural change.

As regards cracks, bit No. 7 is a fairly good specimen. There seems to be no connection between the heated portion and the location of the deepest crack. However, there are numerous small and incipient cracks within the area of structural change.

The most serious cracks in bit No. 8 are, generally speaking, not within the region of structural change but are in the as-rolled section of the bar; the bit would be classed as poor.

A condition similar to that of bit No. 7 is found in bit No. 9; there are few deep cracks in any portion of the specimen. The deepest one, 0.924 mm., is distinctly in the as-rolled section. The bit may be classed as passable.

It will be seen from the foregoing that the bits divide themselves into two classes with respect to cracks: Four of them, Nos. 1, 5, 6, and 8, being

classed as poor to bad, and the remaining five, Nos. 2, 3, 4, 7 and 9, being classed as fair to good. In the former, there is a definite relation between the region of structural change and that of the most prevalent and deepest cracks. In the latter five, there are three in which no definite connection has been found and one in which the authors express a doubt; the remaining one (No. 3) shows an apparent relationship. From such an analysis, the conclusion is that in those bits which are susceptible to cracking, the condition is aggravated by the change in structural condition brought about by the numerous heatings; and when the steel is relatively free from cracks the numerous heatings apparently do not have such a deleterious effect; therefore, it seems reasonable to conclude that the structural change is not the primary cause of the breaks, but is an accessory in the case of defective steel.

It will be noted that the foregoing results cast no direct light on the reason for the greater number of failures occurring in the short lengths than in the long steels. The bits examined were numbered from one to nine in the order of the length of the steels they represent; No. 1 being the starter length and No. 9 the longest length. To obtain definite results bearing on the reason for the failure of the shorter lengths, it would be necessary to examine a large number of each of the lengths and so arrive at the average condition; nevertheless, one can readily see how the development through working of the cracks, which are shown to exist in these steels, would in time result in considerable breakage of the steels longest in use; in other words, of the short lengths of large gage.

Typical shallow and deep cracks are shown at a magnification of 100 diameters in Fig. 3, 4, 5, and 6. The cracks shown by Figs. 4 and 5 are filled with a foreign substance. This can hardly be slag present in the metal before it was rolled into the bar; such slag would, no doubt, be rolled out parallel to the direction of working. This foreign substance is probably rock dust carried there by the water or iron oxide or a mixture of the two. This filling matter is more prevalent in cracks found within the region of structural change, in which event it is doubtlessly iron oxide that formed during the heating of this portion incidental to sharpening and treating. Certain of the cracks appear as discontinuous areas filled with some foreign matter; such cracks are actually continuous, appearing as isolated patches only because no sectioning in a plane could follow their tortuous path.

In Fig. 3, there are cracks extending at right angles to the main crack and therefore parallel to the axis of the steel; these tributary cracks are probably caused by the corroding action of the water that found its way into the large crack and there attacked the more impure portions of the steel, which had been rolled out in a direction parallel to the water hole during the fabrication of the drill steel.



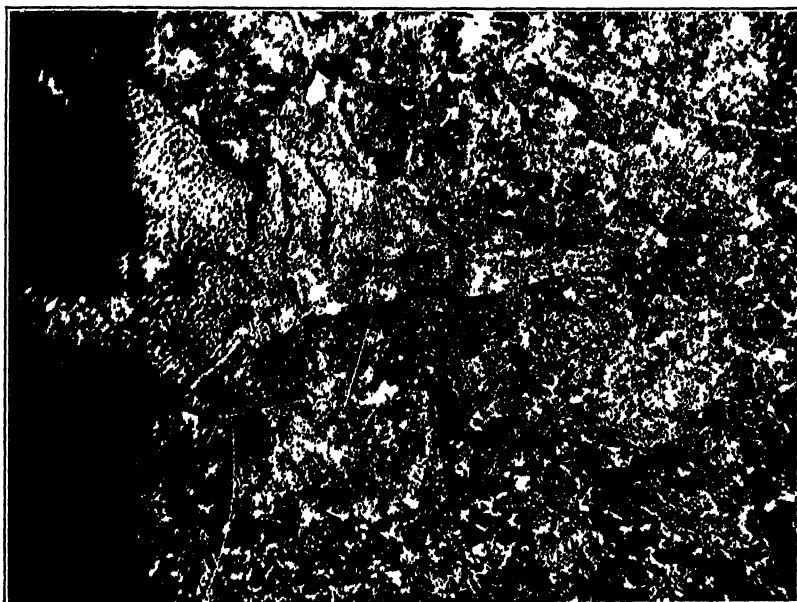
(a)



(b)



(a)



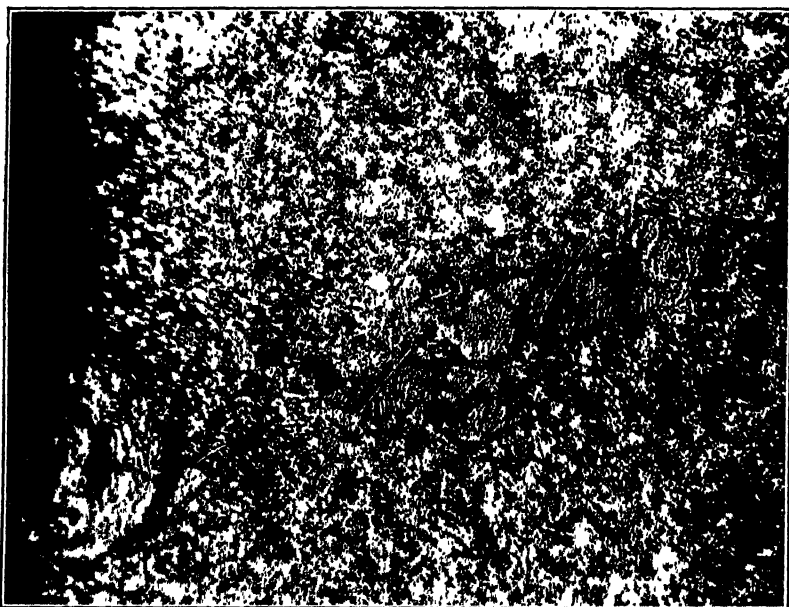
(b)

FIG. 4.—TYPICAL CRACKS IN DRILL STEELS.  $\times 140$ . (a) UNETCHED; (b) ETCHED.





(a)



(b)

FIG. 5.—TYPICAL CRACKS IN DRILL STEELS.  $\times 140$ . (a) UNETCHED; (b) ETCHED.

The edge along the water hole of the steels is seldom straight, being undulated and often serrated, and it is in the bottom of these undulations and serrations that the cracks start. To determine to what extent these defects were present in steels that had not been used in drilling, pieces from six "as-rolled" bars of drill steel were sectioned and polished for examination in the same manner as the nine specimens just described. In all, only three incipient cracks were detected, but undulations in

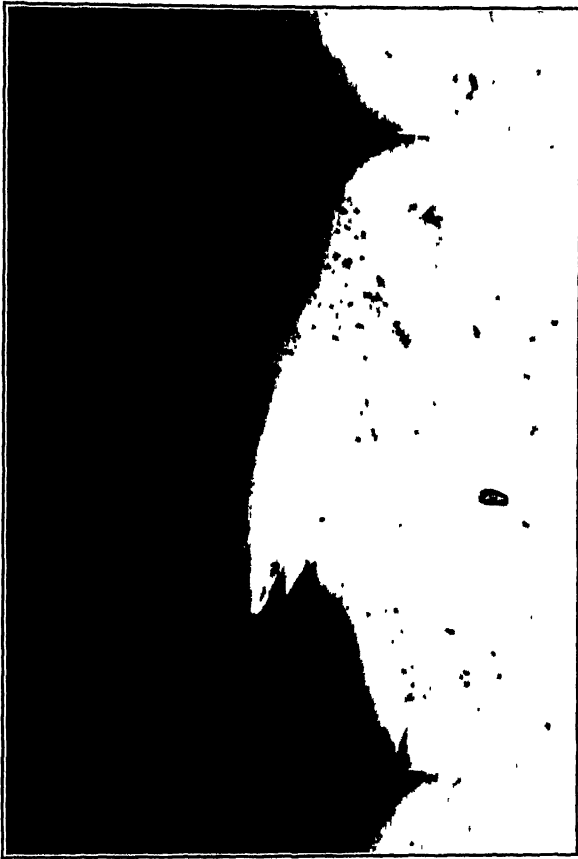


FIG. 6.—TYPICAL SHALLOW CRACKS.  $\times 140$ . UNETCHED.

the water hole were there and the three cracks found appeared to start from the bottom of undulations. The fact that the cracks were found to be more prevalent in used steel than in the "as-rolled" bars indicated that they are developed in service; and the close association of the cracks with undulations and serrations in the wall of the water hole seems to indicate that the method used in producing the water hole is a predisposing cause.

## EFFECT OF CRACKS

As long as there are so many users of steel who are willing to attribute the failure of steel to "crystallization from fatigue" there will continue to be great difficulty in arriving at the true cause of failure in many cases. Steel is naturally crystalline and it is rarely, if ever, found to be anything else; certainly it has never been demonstrated that an amorphous condition can be produced in steel. Some investigators believe that thin films of amorphous metal are formed in steel by stressing beyond the elastic limit, but such an idea is the opposite of crystallization.

Steel fails from overloading and a piece of steel that is defective is more easily overloaded than a sound piece. To quote Moore<sup>1</sup> "So far we have seen no failure that could not be explained by localized high stress, a crack at a point where one heat treatment stopped and another began, or where there was local faulting, or any of a dozen causes."

It is almost impossible to emphasize too greatly the weakening influence of cracks. Were the effect of a crack merely that of reducing the effective cross-section of the steel bar, such small transverse defects as we have noted would be of little consequence; the effect, however, is more insidious. All blacksmiths are familiar with the fact that a bar of mild steel may be bent cold over an anvil, whereas the same bar when nicked with a set will break off short; this is not merely because the section of the bar has been reduced but because the nick has caused the stresses, due to the hammer blow, to become localized at the base of the nick.

There is practically unanimity of opinion among investigators of the phenomenon of fatigue, that failure results from a localization of stress. It was first elaborated by Gilchrist,<sup>2</sup> who stated that fracture under repeated stress was caused by the statical breaking limit being exceeded at one point only. From this point, when once started, rupture spreads at first rapidly then more slowly, sometimes continuing to complete separation of the two parts of the bar, but occasionally stopping short of complete rupture. He states furthermore that the raising of the stress at the point when fracture commenced was caused by an irregularity in the bar, which might be an irregularity or discontinuity in the metal either on the surface or in the body of the bar, and that a bar of uniform strength whose surface was perfectly smooth with no sharp corners in the longitudinal configuration and the structure of which was perfectly homogeneous would endure without breaking, an indefinite number of repetitions of stress varying between zero and a value near to the breaking point.

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<sup>1</sup> H. F. Moore: Investigation of Fatigue of Metals under Stress. *Trans.* (1921) 66, 807.

<sup>2</sup> *The Engineer* (London) 90, 203.

Coker,<sup>3</sup> working with transparent models, has shown, in a graphical manner, that in regions of abrupt change of cross-section under stress there is a localization of stress that in many cases very considerably exceeds the stress per unit area computed for the cross-section as a whole. Moore<sup>4</sup> has found that it is possible to subject a homogeneous steel of 0.9 per cent. carbon to one hundred million reversals of stress as high as the elastic limit of the steel with no sign of failure.

Slight imperfections, such as an 0.003-in. groove, have reduced the fatigue-resisting properties of a steel 40 per cent. and tool marks lead to early failure of parts. The cracks in the water hole of drill steel, insignificant though they may appear, are really potent sources of failure.

### MITIGATION OF THE EFFECTS OF CRACKS

Every piece of steel that has been subjected to an operation involving heating and cooling has been heat treated. The heat treatment may or may not have been beneficial, nevertheless the crystalline structure has been improved or injured according to the manner in which the heating and cooling operations have been conducted. Therefore, the conditions under which steel is heated and cooled should always be governed so as to produce metal in the best condition possible for the purpose for which it is intended. Merely to heat steel to any temperature at which it can readily be worked, to work it with no regard to the temperature at which cooling will commence, and then to fail to consider the rate at which the metal will cool, is to invite trouble.

Steel is a mixture of iron and cementite, and the mixture can be coarse or fine, homogeneous, or heterogeneous, according to the manner in which it is treated. If steel already contains the defects we have found, and if it is claimed that these defects cannot be entirely eliminated, it becomes imperative that the condition of the metal be such that it will best withstand their weakening influence.

The Charpy or the Izod impact test, in which a notch is purposely introduced in the specimen to determine the resistance of the metal to stresses applied when it is in that condition, gives some indication of the value of heat treatment in increasing the resistance of steel to failure under shock in spite of the presence of a notch. Results reported by Howe, Foley and Winlock<sup>5</sup> showed, in general, that very slow rates of cooling from above the critical range produced the lowest notched impact-resistance values, whereas a relatively rapid rate, such as that obtained

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<sup>3</sup> E. G. Coker: *General Electric Review*, 1920-21-22.

<sup>4</sup> *Loc. cit.* Also Moore and Kommers: *An Investigation of the Fatigue of Metals*. Univ. of Ill. *Bull.* (1921) No. 124.

<sup>5</sup> Influence of Temperature, Time and Rate of Cooling on Physical Properties of Carbon Steel. *Trans.* (1923) 69, 722.

by an air blast, produced a stronger steel with a much higher notched impact value.

As there are probably few cracks, of the kind we have been discussing, present in new steel and if, as we suggest, it is the unevenness of the water-hole surface that leads to their formation during service, it seems to us that steel rendered tougher might well withstand service conditions without the formation of these cracks that later in the life of the steel lead to failure. Whether or not it is advisable to treat every bar of drill steel depends, of course, on relative cost. What expense does breakage of drill steel incur? Would the higher cost of properly annealed drill steel pay for itself?

### SUMMARY

Mine drill steels were examined to detect the cause of the prevalence of failures at the bit end of short steels of large gage at a particular mine.

Transverse cracks along the water hole were found.

In those steels that contained the greatest number of defects a relationship apparently existed between the location of the most serious cracks and the point of structural change produced in heating the bit for sharpening and hardening. No such relationship prevailed in the steels showing the fewest cracks.

The deleterious effect of the change in structure caused by heating the bit is thought to cause failure there in those steels that are already predisposed to breaking by the presence of the transverse cracks.

The gradual spreading of cracks during the period of life of the drill steel leads to breakage occurring more frequently in the short lengths, which are usually the steels that have been longest in service, the greater proportion of new steels among those of greatest length materially reducing the breakage percentage.

New steels are found to contain very few actual cracks but the surface of the water hole is quite uneven, and in used steels the cracks seem to originate at the base of such undulations or serrations. These irregularities are, therefore, thought to be a predisposing cause of cracks.

## The Trend in the Science of Metals\*

BY ZAY JEFFRIES, CLEVELAND, OHIO

EACH generation accepts the developments of the preceding generations without full appreciation of the difficulties that had to be overcome or of the effect of any given development on society. Today, the production of pig iron is the yardstick with which general industrial health and progress are measured. So natural and logical does this seem to us, that it is difficult to picture conditions prior to the fourteenth century when pig iron was unknown. Not only was pig iron unknown but iron or steel could not be melted and poured into castings; all iron and steel articles were forged from sponge iron.

All castings, as well as many worked articles, were made of non-ferrous metals or alloys. In many parts of the world, over long periods of time, not only was the annual exchange value of non-ferrous metals greater than that of iron and steel, but their combined tonnage was greater. At present, the value of the pig iron produced in a year is of the same order of magnitude as that of all non-ferrous metals combined; the tonnage of pig iron is, however, about twenty times that of all non-ferrous metals combined.

Owing to lack of records, we will probably never know the relative importance of the various metals at all periods in historic times. A certain conclusion is that the iron and steel industry, since the discovery of pig iron and the cheap methods of converting it into steel, has grown at a much more rapid rate than the non-ferrous metal industries. Notwithstanding their fundamental fitness for man's needs, iron and steel owe their importance in no small degree to the low cost of production. The low cost was a result of increased knowledge of the production appliances and of the metallurgical processes. This increased knowledge is the key to our modern industrial civilization.

It will remain for future generations to determine whether there is now going on a gradual change toward greater importance of the non-ferrous metals, as compared to iron and steel. The world's pig iron production in 1920 was slightly more than twice what it was in 1890, whereas the non-ferrous metals production in 1920 was about two and one-half times that in 1890. Every non-ferrous metal industry has shown marked growth during the last thirty years. During this period, the production of cop-

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\* Third Annual Lecture of the Institute of Metals Division, the American Institute of Mining and Metallurgical Engineers, at the New York Meeting, February, 1924.

per, nickel, and aluminum has increased at a much faster rate than that of pig iron.

Assuming different degrees of fitness for industrial uses, the relative importance of the various metals depends on:

1. Cost of production;
2. Knowledge of properties and shapes desired for industrial uses;
3. The state of the science of metals, *i. e.*, the knowledge of the properties of metals and their alloys and of the processes of fabrication.

In the growth of any particular metal industry, all of these factors are inter-related. A revolutionary discovery in any one of these fields may result in a marked increase in demand; also increased knowledge of any metal may greatly change its rate of growth.

The Institute of Metals Division is principally interested in the third item, which is referred to as the science of metals. We will confine the discussion this afternoon to certain aspects of this subject.

Many physical and mechanical properties must be considered in the selection of metals and alloys for industrial uses; namely, resistance to corrosion, electrical conductivity, magnetic properties, melting point, vapor pressure, bearing qualities, machinability, coefficient of expansion, strength, elastic limit, hardness, elongation and reduction of area after rupture by tension, resistance to repeated stresses, resistance to impact, etc. Sometimes, a number of these properties must be within specified limits in the same material; again some property, not specified, may be essential in order to fabricate a desired article. If we consider the various properties of metals from the standpoint of their contribution to usefulness, there is probably good agreement that plasticity and hardness rank first. If we examine all the uses of metals, we can find no considerable use in which either or both of these properties is an unimportant factor. Drawn copper wire, for example, may be used for a conductor of electricity in places where its hardness or even its plasticity may not be an important factor, but if it were not plastic it could not have been drawn into wire. The use of cast iron would be very limited if it were as soft as lead. Furthermore, the high compressive strength and the machinability of cast iron are due, in a large measure, to the plasticity of the main constituent—ferrite. The specifications for structural metals nearly always demand certain tensile strengths and elongations. In mechanical working operations, resistance to permanent deformation and capacity for being permanently deformed without rupture are major factors. Important as the subject of hardness is, it has received so much attention during the last few years that we would not be warranted in giving it further consideration today.

Each year, the chances are becoming less for the layman to make signal advances in the science of metals. The trend in the science is in the direction of atomic physics. The old tools are not being discarded

but are being used more and with better understanding. New tools are being developed which have already greatly enriched our knowledge and promise even greater things in the future. New developments are now often the result of laborious researches involving a profound study in fields that have been worked over, on the surface, many times; the tools available permit us to make a more profound study than could have been made even two decades ago. I have selected for discussion two subjects, namely, diffusion in the solid state and plasticity. The knowledge on these subjects has been greatly augmented by the new physical methods of attack. When dealing with fundamentals, there is no sharp distinction between iron and steel and the non-ferrous metals, I will therefore take some examples from each of these two major fields.

At the outset, I wish to express my indebtedness to my associates, Messrs. Archer, Sykes, Gladding, Karrer, Bain, Tarasov, and Doran.

#### DIFFUSION IN THE SOLID STATE

The diffusion of carbon into solid iron at an orange heat has been practiced for thousands of years, but it is only in recent times that this process has been crudely understood. Two notable researches on diffusion in the solid state are those of Roberts-Austen,<sup>1</sup> who studied the rate of diffusion of gold from a lead-gold alloy into pure lead, and Bruni and Meneghini,<sup>2</sup> who studied the interdiffusion of copper and nickel. The experiments on copper and nickel are typical cases of diffusion in the solid state. A nickel wire 0.5 mm. in diameter was coated electrolytically with sufficient copper to make the mixture correspond to 59 per cent. copper and 41 per cent. nickel. The compound wire was heated in a hydrogen atmosphere to 1000° C. and the electrical conductivity was measured from time to time. The progress of diffusion was followed by the decrease in conductivity. The conductivity reached a constant value after 140 hr., which value was the same as that of a homogeneous alloy of the same composition. The color of the copper had changed from red to white and other tests confirmed the conclusion that both core and shell were of the same composition after the long heating. Copper and nickel form an unbroken series of solid solutions. It is a requirement in such solid-solution alloy systems that either element should diffuse in the other in the solid state.

In any case of diffusion in the solid state, there is usually some low temperature at which diffusion will not take place; or, what practically amounts to the same thing, a temperature at which the rate of diffusion is imperceptible. The rate of diffusion increases rapidly with rise in tem-

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<sup>1</sup> *Phil. Trans.* (1896) 187A, 383.

<sup>2</sup> *Int. Zeit. für Metall.* (1912) 2, 26; Desch: Diffusion in Solids. *Reports on the State of Science* (1912) 358.



perature. Roberts-Austen found that the diffusion of gold from an alloy of lead and gold into pure lead was 400 times more rapid at 200° C. than at 100° C. The increase in rate of diffusion with rise in temperature is so universal that it may be regarded as one of the diffusion laws.

The rates vary, however, in specific instances. From the experiments on copper and nickel cited above, it is evident that the copper atoms must have traveled half the diameter of the nickel wire, or 0.025 cm. in 140 hr. Reduced to other units, it is found that the faster moving copper atoms advanced about two atom diameters per second. Under certain conditions, the rate of penetration of carbon into steel is 100 times as fast as copper in nickel, or 200 atom diameters per second. This rate can be accelerated by rise, or retarded by decrease, in temperature. The rate of vibration of the atoms due to temperature is something over 1,000,000,000,000 times per second. It is therefore evident that, in the case of the copper-nickel alloy, there would be on the order of 1,000,000,000,000 vibrations due to temperature to each movement of a copper atom a distance of one atom diameter. In the iron-carbon case, there would be on the order of 10,000,000,000 temperature vibrations to each movement of a carbon atom a distance of one atom diameter. It is thus seen that the movement of solute atoms in solid diffusion is relatively sluggish.

Recently Langmuir and Dushman\* have made a study of the diffusion of thorium in tungsten. The source of the thorium is thorium dioxide (thoria) about 0.75 per cent. of which is added to the tungsten oxide before the latter is reduced by hydrogen to tungsten powder. Thoria is not reduced by hydrogen and, consequently, remains in the tungsten almost entirely as the oxide. It was formerly thought that the thoria remained completely unreduced. Thanks to Langmuir, it is now known that a very small amount is reduced to metallic thorium. Tungsten containing as little as one part of thorium in 40,000 would defy even detection by any ordinary method. The thorium, however, diffuses to the surface and at temperatures near 1800° C. an adsorbed layer of thorium atoms forms on the surface of the tungsten filament. The electron emission from thorium is much greater than from tungsten and it is the surface layer of atoms that controls the electron emission. A tungsten filament coated with a layer of thorium atoms has, therefore, approximately the emission of a thorium filament at the same temperature. At certain temperatures, a filament with an adsorbed layer of thorium atoms will have many thousand times the electron emission of a pure tungsten filament at the same temperature. Incidentally, the electron emission is the basis of

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\* Langmuir: The Electron Emission from Thoriated Tungsten Filaments. *Phys. Rev.* (1923) 22, 357.

Dushman and Langmuir: *Phys. Rev.* (1922) 20, 113.

current flow between filament and plate in vacuum tubes used in radio detection and amplification and for other purposes.

This case of diffusion in the solid state is not only important because of its great practical use but because of the method of study, which provides a means of determining the state of combination of the foreign atoms when other methods fail, and because of the example of how one property of a metal is increased many thousand times by the presence of as little of another substance as one part in 40,000.

In order for diffusion to take place, there must be a concentration gradient. In the examples discussed, the concentration gradients were such as to cause a flow of foreign atoms in certain general directions. These cases offer the best means for quantitative study of diffusion and, hence, for a mathematical treatment, such as that of Langmuir and Dushman. There are other cases of diffusion, most important in the heat treatment of metals, which relate to the change in size of discrete particles of one or more constituents within a metallic matrix. Concentration gradients exist in all directions from particle to particle so that a quantitative study of either the magnitude of the gradient or the rate of diffusion is very difficult. Change in particle size is, however, certain evidence of diffusion.

An important example of change of particle size in the solid state is that of an alloy of aluminum, copper, and magnesium. Merica, Waltenberg and Scott<sup>4</sup> were the first to attribute the hardening of duralumin to the precipitation of small hard particles from a supersaturated solid solution. The supersaturated solution is produced by saturating at a high temperature followed by quenching to prevent precipitation during cooling. Precipitation and particle growth take place slowly at room temperature. The first precipitation is accompanied by hardening and increased strength and decreased plasticity. When the particles reach a certain size, called critical size (critical dispersion), the hardness reaches a maximum and the plasticity a minimum. With further increase in particle size, the hardness decreases and the plasticity increases. Apparently, at each temperature, the particles will not grow beyond a certain size, which is larger the higher the temperature. Duralumin will never, to the best of our knowledge, soften at ordinary temperatures. At 300°C., the particles grow to such a size that the hardness of the alloy may be reduced to half that of the hardest condition. Let us consider the causes of these phenomena.

Langmuir and Dushman found that the rate of diffusion of thorium in tungsten was negligible below 1200°C. The atomic volume of tungsten is 9.5 and that of thorium is 19.1. These relative volumes are shown as spheres in Fig. 1. As the temperature increases the diffusivity increases

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<sup>4</sup> Heat Treatment and Constitution of Duralumin. *Trans.* (1920) 64, 41.

rapidly. With a small amount of silicon present, magnesium, with an atomic volume of 14.3, diffuses at room temperature in aluminum, which has an atomic volume of 10. Diffusion will not take place at the temperature of liquid air, 190° C. The relative sizes of these atoms in spherical form are shown in Fig. 2. Carbon will diffuse in iron at room temperature. The carbon atom is the smallest of all of the elements solid at

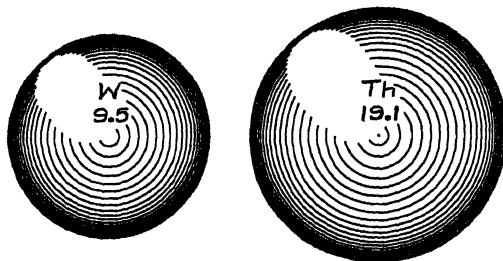


FIG. 1.—RELATIVE SIZES OF THORIUM AND TUNGSTEN ATOMS.

ordinary temperatures. Its atomic volume, in diamond, is 3.42 and that of iron is 7.1. We have considerable evidence showing that tungsten in high-speed steel will not diffuse to any substantial extent in alpha iron below about 450° C. and that its rate of diffusion increases rapidly above this temperature.<sup>5</sup> The relative atomic volumes of the principal elements of high-speed steel are shown in Fig. 3. The relative sizes of atoms are

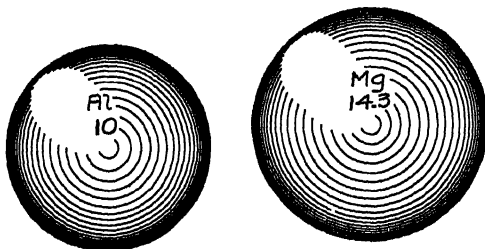


FIG. 2.—RELATIVE SIZES OF ALUMINUM AND MAGNESIUM ATOMS.

always important, and sometimes controlling, factors in diffusion in the solid state. A very large atom might not be able to diffuse in a small atom lattice at any temperature.

There must be a "diffusion force" and a "diffusion resistance." While diffusion is progressing, the force must be greater than the resistance. When there is no diffusion, either the force and resistance are equal, which is the condition for equilibrium, or the resistance must be greater than the force. Each of these factors is obviously a complex.

<sup>5</sup> Bain and Jeffries: Cause of Red Hardness of High-speed Steel. *Iron Age* (Sept. 27, 1923) 805.

Diffusion force probably depends largely on: (1) Concentration gradient, and (2) relative attractive forces between like and unlike atoms.

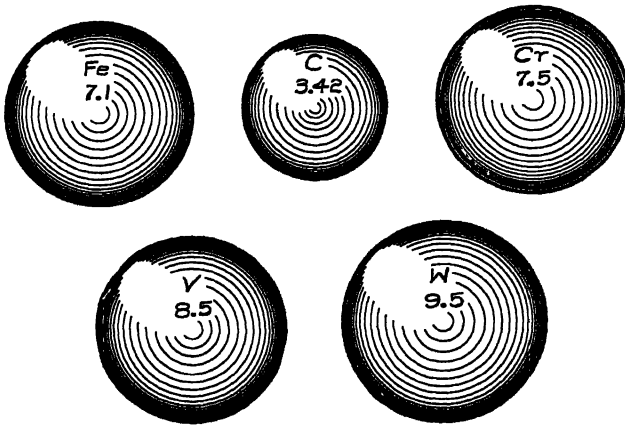


FIG. 3.—RELATIVE SIZES OF ATOMS OF PRINCIPAL ELEMENTS IN HIGH-SPEED STEEL.

The greater the concentration gradient and the more the mutual attraction of the unlike atoms differs from that of the like atoms the greater should be the diffusion force.

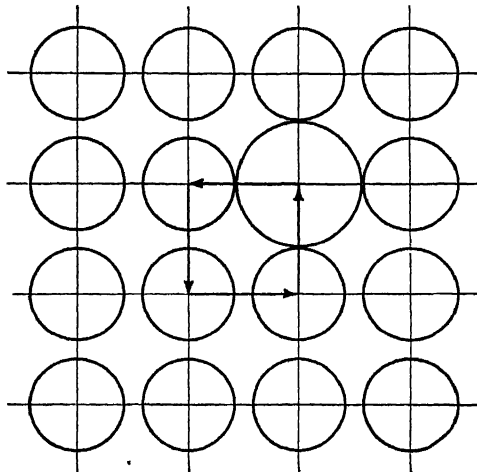


FIG. 4.—SCHEMATIC CONCEPTION OF DIFFUSION IN CRYSTALLINE LATTICE.

Diffusion resistance probably depends largely on: (1) Temperature, (2) atom size, and (3) dimensions and type of space lattice.

It is easy to understand why the diffusion resistance would be lower the higher the temperature; the space lattice becomes larger and the force

required to move the atoms relative to one another is decreased. It is not easy, however, to comprehend why diffusion in the solid state takes place at all. The atoms are very resistant to deformation, as evidenced by the large forces required to deform metals elastically. Steel stressed to 300,000 lb. per sq. in., elastically, in tension has its space lattice extended only 1 per cent. With such great forces required for so little deformation, it is difficult to understand how two atoms could exchange places. Langmuir has proposed a mechanism that is quite satisfying. Fig. 4 shows schematically a group of atoms of one size enclosing a larger foreign atom. Assuming the matrix atoms to represent tungsten, the larger atom is about the proper size to represent thorium. The concentration gradient is such as to produce a diffusion force from right to left. The movement is effected by a rotation of four adjacent atoms simultaneously. It is obvious that such rotation can take place without greatly disturbing adjacent atoms. The rotation may not always involve four atoms.

Rosenhain<sup>6</sup> reports that diffusion is more sluggish in metals having space lattices of low symmetry than in those with high symmetry. It is true that the rate of diffusion of aluminum in the magnesium space lattice is slow. This accords with Langmuir's conception of the mechanism of diffusion because diffusion would be most rapid on those planes on which mechanical slip is easy. Magnesium crystallizes with a hexagonal space lattice of low symmetry. This mechanism also fits in with the known fact that diffusion is relatively easy in amorphous, as compared to crystalline, materials. In amorphous materials, the rotational movement would take place in any direction and the atoms or molecules probably have rotational movement in addition to that due to temperature.

To return to the matter of particle growth, in order for diffusion to take place there must be a concentration gradient. Ostwald<sup>7</sup> seems to be responsible for the idea that at a given temperature the concentration gradient is due to the greater solubility of the particles the smaller the size. Of course, in no case, even after equilibrium is established, are all of the particles the same size. As particle growth represents increase in size and decrease in number of the particles, it is obvious that the smaller particles must be completely dissolved to furnish material for the growth of the larger ones. Later results indicate<sup>8</sup> that as the average size of the particles become larger a greater difference in size is necessary to produce a given differential solubility. Therefore the most favorable condition for a high concentration gradient, and hence high diffusion force, is that of a very fine dispersion of particles of different sizes. Con-

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<sup>6</sup> Institute of Metals *Trans.* (1923) **30**, 3.

<sup>7</sup> *Zeit. für Phys. Chem.* (1900) **34**, 495.

<sup>8</sup> Jeffries and Archer: *Chem. & Met. Eng.* (Mar. 8, 1922).

sider, for example, freshly quenched steel at  $100^{\circ}\text{C}$ . The particles of precipitated cementite are very small and the differences in particle size will produce high concentration gradients and, hence, high diffusion force. The temperature is low so the diffusion resistance is also high. When these forces are balanced, the particle size is still very small. Now, if the temperature is raised a little, the high diffusion force still obtains but the diffusion resistance is lowered. The particles will now grow until the new diffusion force just equals the new resistance and a new equilibrium with a somewhat larger mean particle size is established. This would account for the equilibrium particle size being larger the higher the temperature.

In complex alloys, the different kinds of atoms have different diffusion forces and resistances. In high-speed steel, after quenching, the diffusion forces of the carbon, tungsten, chromium, and vanadium atoms are high. The diffusion resistance is probably less for carbon than for any of the other atoms, because of its small size; at any rate, the carbon diffuses at room temperature forming iron carbide. Iron carbide is not the most stable compound of the elements involved, as evidenced by the preferential formation at a higher temperature (near  $500^{\circ}\text{C}$ .) of a complex carbide containing tungsten. The formation of these compounds demands diffusion because they are the result of crystal formation rather than chemical combination and the formation of a crystal requires a number of each kind of atom. If, owing to the high diffusion resistance of certain of the atoms, the most stable compound cannot form, less stable compounds may form with those atoms that can diffuse. Hence, we may have reactions going on in solid metals governed by availability of atoms rather than by the stability of the resulting compound.

Instances of particle growth in solid metals are much more numerous than we might at first suspect; the number will increase as we find better ways to produce fine particle dispersions. An unusual example is the growth of thoria particles in tungsten. After Langmuir had demonstrated the presence of a minute amount of metallic thorium in tungsten filaments containing thoria, it seemed probable that even this slight solubility of thoria might be sufficient to cause diffusion and particle growth. This was found to be so. Fig. 5 shows the fine dispersion of thoria particles in tungsten produced by heating the briquetted slug at a temperature considerably below the melting point of tungsten. Fig. 6 shows the decrease in number and increase in size of the thoria particles produced by heating at a temperature only slightly below the melting point of tungsten. The particle growth is gradual as the temperature increases. Such growth is significant because it shows the presence of free oxygen as well as free thorium atoms in the tungsten space lattice. The thorium and oxygen atoms probably leave the smaller thoria particles as uncombined atoms and diffuse independently toward the larger particles where recombination takes place. The thoria particle growth has

been observed so many times that there can be no question regarding the point of fact.

A considerable solid solubility within some temperature range and a substantial change in solid solubility with temperature are conditions favorable for reversing the particle size by heat treatment. If, for example, in duralumin the aluminum lattice is just saturated with the alloying elements at the quenching temperature, a sufficient amount of hard compound will precipitate at low temperatures to produce marked changes in properties. These particles can be completely dissolved again by reheating to the quenching temperature. The particle size change is

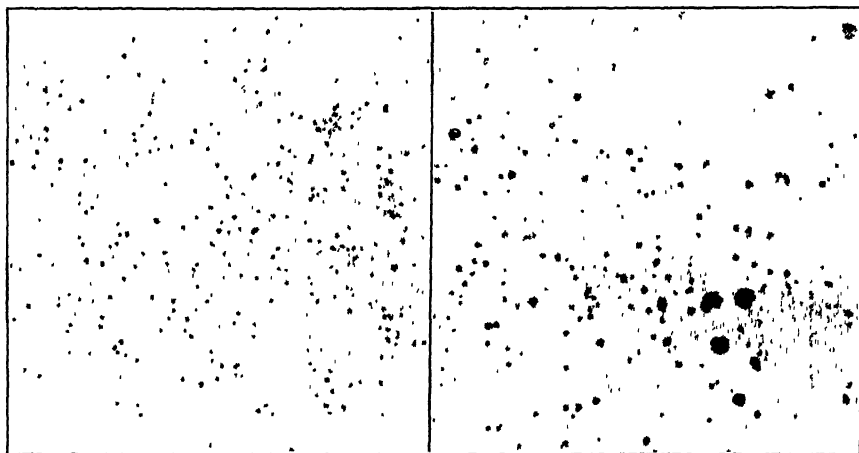


FIG. 5.—TUNGSTEN CONTAINING FINE PARTICLES OF THORIA.  $\times 500$ .

FIG. 6.—THORIA PARTICLES IN TUNGSTEN ENLARGED BY DIFFUSION AT HIGH TEMPERATURE.  $\times 500$ .

a reversible one. If, however, there is an excess of the hard particle constituent above the saturation limit at the quenching temperature, such excess does not enter into the reversible changes.

A point that has not been sufficiently stressed in the past is that the effect of an apparently insignificant solid solubility may be very marked. In the case of thoria in tungsten, there may be 250 times as much thoria present as thorium. If the thoria is initially present as particles smaller than the equilibrium particle size at some high temperature, this minute amount of solid solubility is sufficient to bring the particles up to equilibrium size. Thus a slight solid solubility may affect the size and distribution of hundreds of times the quantity of the material in solution at a given time. In such cases the change in particle size is not reversible. There is a small reversible change confined in magnitude to the actual change in solubility.

With such an example as that of tungsten and thoria, it is not an unfair prediction that hundreds of new examples of particle growth in the solid

state will be discovered in the future and that increased knowledge in this direction will be of great practical value. Part of this value will be due to the direct use of the information but perhaps a greater part will be due to the better understanding of subtle structural changes in metals.

### PLASTICITY OF METALS

In 1899, Ewing and Rosenhain<sup>9</sup> informed the world that plastic deformation of metals takes place by slippage along definite crystallographic planes. The mechanism of flow in a crystalline material was found to be different from that in amorphous materials like glass. The mechanism has been referred to as comparable to increasing the overall length of a deck of cards by sliding some of the cards relative to others.

For about two decades metallographists, and occasionally physicists, have experimented much and conjectured much in an endeavor to throw further light on this phenomenon. Many of the leading metallographists, at some time during the last twenty-five years, have worked on this problem, especially with reference to the change of orientation of crystalline fragments at slip planes. Most of them have arrived at the conclusion that the movement at slip planes takes place without change in orientation of the crystal fragments. It is interesting to note, however, that Mathewson and Phillips<sup>10</sup> leaned toward the view that change of orientation occurs during plastic deformation.

During the last few years this problem has been attacked with the *x*-ray spectrometer and definite answers to some of the contentious questions have been provided. Bain and the speaker<sup>11</sup> showed that a few large crystals of copper or aluminum or tungsten developed fairly random orientations by a moderate amount of working, the work being done at room temperature in the cases of aluminum and copper and above about 1000° C. in the case of tungsten. On reheating above the temperatures of recrystallization, the orientations were still quite random but the grains were fewer in number and larger. This proved beyond any doubt that plastic deformation changes the orientation within the original grains.

Mark, Polanyi, and Schmid,<sup>12</sup> in Germany, studied the deformation of single crystals by means of *x*-ray crystal analysis. They found change of orientation at slip planes produced during the ordinary tensile test in single crystals of zinc. Conditions for maximum elongation of single crystals of zinc were determined. Zinc crystallizes with a hexagonal

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<sup>9</sup> *Phil. Trans.*, 193, 353.

<sup>10</sup> *Trans.* (1916) 54, 608.

<sup>11</sup> *Chem. & Met. Eng.* (Oct. 26, 1921) 775.

<sup>12</sup> *Zeit. für Phys.* (1922) 12, 58.



space lattice and the plane of easiest slip is the base of the unit hexagonal prism. Where this plane makes an angle of approximately  $45^\circ$  with the wire axis, the crystals are very ductile. Single-crystal wires broken in tension at room temperature have shown as much as 600 per cent. elongation; broken at  $205^\circ$  C. elongations up to 1700 per cent. have been obtained. Although zinc is not regarded as a very ductile metal, these values for elongation are the highest of any known metal. Unless the plane of easiest slip is at an opportune angle, with respect to the wire axis, the crystal is relatively brittle. Single-crystal wires of bismuth tested at  $200^\circ$  C. showed up to 300 per cent. elongation. In this case, also, the plane of easiest slip must make an angle with the wire axis of about  $45^\circ$ , or the crystal will be brittle when broken in tension. During the process of elongation of the zinc single crystals, the round wire changed into a flat ribbon; the width of the ribbon was, at first, slightly wider than the original diameter of the wire. Slip occurred in a plane about  $45^\circ$  from the wire axis and extended across the whole cross-section of the wire in such a manner that the intersection of each slip band with the wire surface formed an ellipse. The slight widening of the ribbon was due to the rotation of the elliptical sections. As the elongation increased the general orientation of the crystal changed so that the angles of the easiest planes of slip became more nearly parallel with the direction of extension.

In order that conclusions too sweeping may not be drawn from these phenomenal results on single crystals, it should be mentioned that all of the wires were less than about 2 mm. in diameter and comparable results might not be expected in large single crystals. Fine tungsten wires composed of single crystals are sometimes ductile at ordinary temperatures but larger single crystals have, so far, proved invariably brittle cold.

Since the discovery of the use of x-rays for crystal analysis by Laue in 1912, and particularly since the development of the so-called "powder method" by Hull,<sup>13</sup> in America, and by Debye and Scherrer, in Germany, there have appeared occasional references to unusual patterns from severely cold-worked metals. Nishikawa and Asahara,<sup>14</sup> for instance, reported the results of their investigation at Cornell University in 1919. Unusual patterns were obtained on copper, silver, tin, cadmium, and thallium. Burger<sup>15</sup> in Holland, in 1921, reported that severely drawn tungsten wire possessed directional orientation of the crystal fragments. A very recent paper by Polanyi and Weissenberg<sup>16</sup> covers the interpretation of some of these unusual x-ray patterns. Work has been done along

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<sup>13</sup> A New Method of X-ray Crystal Analysis. *Phys. Rev.*, 10, 661.

<sup>14</sup> *Phys. Rev.* (1920) 15, 38.

<sup>15</sup> *Physika* (1921) 1, 214.

<sup>16</sup> *Zeit. für Tech. Physik* (1923) 4, 199.

these general lines in the Cleveland Wire Division laboratories of the National Lamp Works of the General Electric Co. during the last few years, by E. C. Bain and A. B. Gladding, and more recently also by Dr. E. Karrer, under the direction of the speaker. We have paralleled some of the work of Polanyi and Weissenberg and have obtained some results they have not reported on. Our results agree, in general, with theirs as regards the structure of severely cold-worked metals. We have

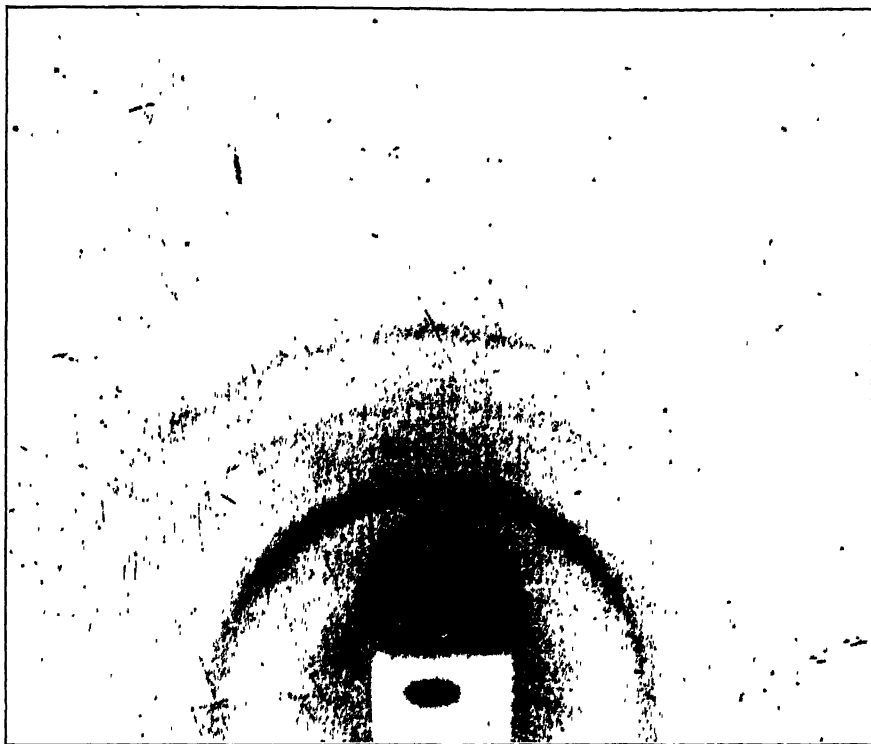


FIG. 7.—DIFFRACTION PATTERN OF POWDERED TUNGSTEN.

arrived at somewhat different views, however, with respect to the structures of metals that have been severely cold worked and have then been recrystallized. Inasmuch as this method of study is, so far, the only one known that will give definite answers to questions of the orientation of submicroscopic crystal fragments some actual results will be considered.

The basis of the study is the powder method of crystal analysis. A fine-grained powder or fine-grained solid material with randomly oriented grains diffracts simultaneously  $x$ -rays from all possible kinds of crystallo-

graphic planes. Fig. 7 is the pattern from tungsten powder produced on a flat film, a little more than half of the diffraction pattern being shown. Tungsten has a body-centered cubic space lattice. The black spot near the bottom center of the figure is produced by the primary  $x$ -ray beam. This is referred to as the origin. The farther apart the crystallographic planes are the closer to the origin will be the diffraction line. Incidentally the farther apart the planes are, the greater is the atomic concentration on the plane and the easier is the slip due to external loading.

The planes are usually designated by their Miller indices. Fig. 8 is one of the 110 planes of a body-centered cubic space lattice. The unit cube of this lattice has an atom at each corner and one in the center of the cube. The length of a side of the unit cube is the unit of measurement used in the Miller indices. The Miller indices are the ratios, expressed in whole numbers and zero, of the reciprocals of the intercepts of a plane on

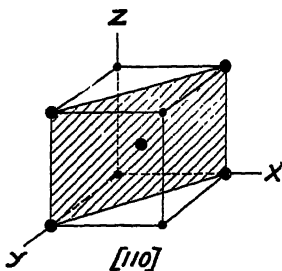


FIG. 8.—ONE OF 110 PLANES IN BODY-CENTERED CUBIC-SPACE LATTICE.

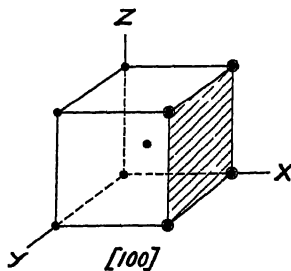


FIG. 9.—ONE OF 100 PLANES IN BODY-CENTERED CUBIC-SPACE LATTICE.

the major axes of the crystal system. In cubic crystals, the axes are the  $x$ ,  $y$ , and  $z$  axes as used in solid geometry. The 110 planes shown in Fig. 8, for example, would intersect the  $x$  and  $y$  axes at unit distance from the origin and would be parallel to the  $z$  axis. The plane is cross hatched and the encircled atoms are on the plane. The Miller indices as used here refer to a family of planes. Not only do the 110 planes include all individual parallel planes with the same atomic spacings but also five more sets of planes having the same atomic spacings making specific angles with one another. The ratios of the reciprocals of the intercepts are expressed in whole numbers and zero because all sets of parallel planes with significant atomic concentration can be designated in this way without resorting to the use of a large integer.

The first line in Fig. 7 is the  $x$ -ray diffraction of the 110 planes. The following table gives the Miller indices of the planes in the body-centered space lattice that diffract the first six lines of the  $x$ -ray pattern and the number of cooperating planes of each type:

Number of Diffraction Line from Origin in X-ray Pattern for Body-centered Cubic Lattice	Miller Index	Number of Cooperating Planes
1	110	6
2	100	3
3	112	12
4	110 (2)	6
5	130	12
6	111	4

It will be noted that the 110 planes appear twice. The first line is due to the first order diffraction and the fourth line to the second order

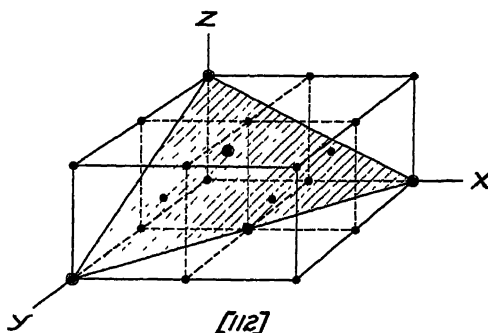


FIG. 10.—ONE OF 112 PLANES IN BODY-CENTERED CUBIC-SPACE LATTICE.

diffraction. The other planes are shown diagrammatically in Figs. 9 to 12, inclusive.

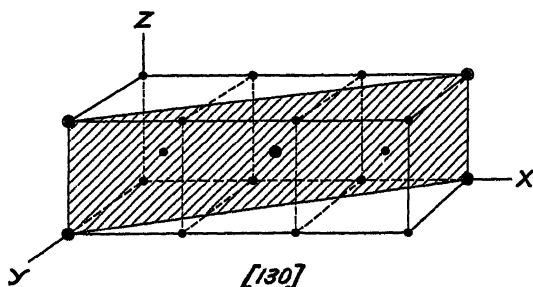


FIG. 11.—ONE OF 130 PLANES IN BODY-CENTERED CUBIC-SPACE LATTICE.

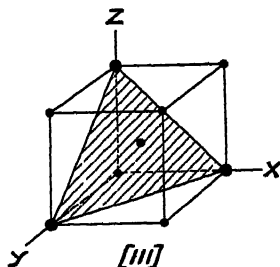


FIG. 12.—ONE OF 111 PLANES IN BODY-CENTERED CUBIC-SPACE LATTICE.

The diffraction pattern of tungsten powder is taken as a standard, as regards the intensity of exposure at any part of a line. Because of the elliptical shape of the x-ray beam, the lines are narrower and darker above the origin than in the horizontal positions.

Fig. 13 is the pattern given by a bundle of severely drawn tungsten wires, mounted parallel to one another with their axes in a horizontal position and perpendicular to the  $x$ -ray beam. The original ingot was a little less than  $\frac{3}{8}$  in. square and the final wire was 0.0006 in. in diameter. This corresponds to a reduction in area by mechanical working of 99.9997 per cent. There are only three spots in the first diffraction line, showing that a limited number of directions of orientations of the 110 planes is present. If certain of the planes are oriented in definite directions, the



FIG. 13.—DIFFRACTION PATTERN OF SEVERELY DRAWN TUNGSTEN WIRE.

positions of all other planes are fixed; it is, therefore, only necessary to study the first two or three diffraction lines to determine the orientations. The crystal fragments of severely drawn tungsten wire are oriented in a definite manner. The preferred arrangement of the crystalline particles is shown schematically in Fig. 14. One set of 110 planes is in the wire cross-section and one set of 100 (cube face) planes is in the wire surface. The other two 100 planes make angles of  $45^\circ$  with the axis of the wire with their line of intersection on a radius of the wire cross-section. The deviations from the preferred orientations are not sufficient to produce additional diffraction spots. In other words, all the spots in Fig. 13 were produced by the preferred orientations.

Some of this wire was heated to a temperature high enough to cause recrystallization; Fig. 15 is the resulting pattern. The pattern is the same as that of the as-drawn sample, showing that no new orientations

were developed on heating. It is not to be concluded that the properties of the as-drawn and recrystallized wires are the same or that their microstructures are similar. In the as-drawn wire, no two adjacent sections around the circumference would have the same orientation. In the recrystallized wire, the orientation is uniform within any recrystallized grain; these grains are large enough to be seen under the microscope. In any of the recrystallized grains, one of the 100 faces will be parallel with the wire axis. The 100 planes in adjacent grains must make different angles with an arbitrarily chosen wire diameter.

Fig. 16 is the pattern from a molybdenum strip rolled, partly hot and partly cold from about  $\frac{3}{8}$  in. thick to 0.004 in. thick. Many orientations are absent. The tendency toward selective orientation is shown. The prevalent positions of the crystal fragments are such as would be produced if a shell of the as-drawn tungsten wire could be removed and flattened. The diffraction spots are largely produced by planes that deviate from these preferred positions. The spots from the 110 planes are due to a deviation of about  $10^\circ$  and the spots from the 100 planes to a deviation of about  $13^\circ$  from the preferred positions. It will be noted that there is no spot on the first diffraction line at the left of the origin. Mr. Gladding calculated that if the surface of the molybdenum strip were tilted about  $10^\circ$  from the original position the crystal fragments in the preferred direction of orientation would produce a spot at this place on the film. Fig. 17 shows how accurate was his prediction.

Some of the molybdenum strip was annealed at  $1050^\circ \text{C.}$ ; Fig. 18 represents the x-ray pattern. The as-rolled strip was set in the holder so that the direction of rolling was horizontal whereas the annealed strip, shown in Fig. 18, was placed with the direction of rolling vertical. The spots in the annealed sample correspond with those in the as-rolled sample, showing that recrystallization at a low temperature has produced no new orientations. A piece of the molybdenum strip was heated to  $1600^\circ \text{C.}$ ; Fig. 19 is the resulting x-ray pattern. The grains were large enough to show the characteristic individual diffraction but the selective orientations persist.

Although the molybdenum was not rolled far enough to produce uniform orientation of the crystal fragments, as in the case of the drawn

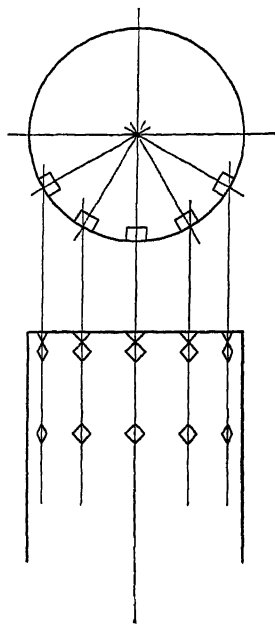


FIG. 14.—DIAGRAM SHOWING SCHEMATICALLY ORIENTATIONS OF CRYSTAL FRAGMENTS IN SEVERELY DRAWN TUNGSTEN WIRE.



FIG. 15.—DIFFRACTION PATTERN OF TUNGSTEN WIRE SEVERELY DRAWN AND THEN RECRYSTALLIZED.



FIG. 16.—DIFFRACTION PATTERN OF ROLLED MOLYBDENUM STRIP.



FIG. 17.—DIFFRACTION PATTERN OF ROLLED MOLYBDENUM STRIP; STRIP PLACED AT SLIGHT ANGLE TO X-RAY BEAM.



FIG. 18.—DIFFRACTION PATTERN OF ROLLED MOLYBDENUM STRIP AFTER ANNEALING AT 1050° C.



tungsten wire, the prevailing orientations are those shown in Fig. 20. One of the 100 planes is parallel with the surface and the other two are normal to the surface and make angles of  $45^\circ$  with the direction of rolling.



FIG. 19.—DIFFRACTION PATTERN OF ROLLED MOLYBDENUM STRIP AFTER ANNEALING AT  $1600^\circ$  C.

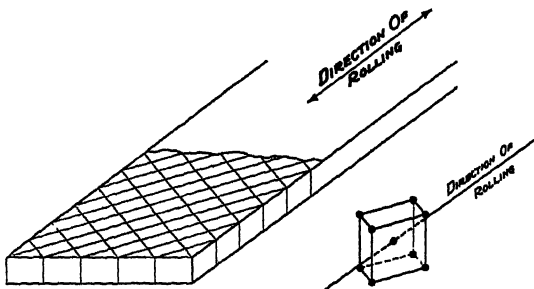


FIG. 20.—PREFERRED ORIENTATION OF GRAIN FRAGMENTS IN SEVERELY ROLLED MOLYBDENUM STRIP.

Fig. 21 is an  $x$ -ray pattern of cold-rolled Armco iron strip. The directional orientations are pronounced but not as marked as in the

molybdenum strip. A piece of this iron was heated to  $800^{\circ}\text{C}.$ , and still showed directional orientation. A piece of the cold-rolled iron was heated to  $950^{\circ}\text{C}.$  and cooled rapidly; Fig. 22 is its *x-ray* pattern. The grains are not sufficiently numerous to do more than indicate the positions of the diffraction lines but all suggestion of directional orientation has been eliminated. From these results, we come to the conclusion that the allotropic transformation in iron at  $A_3$  produces new and random orientations. This conclusion was confirmed by quenching a 0.3-per cent. carbon steel from  $900^{\circ}\text{C}.$ ; the diffraction pattern of this steel is shown in Fig. 23. The pattern is exactly similar to that of a powder. The sample

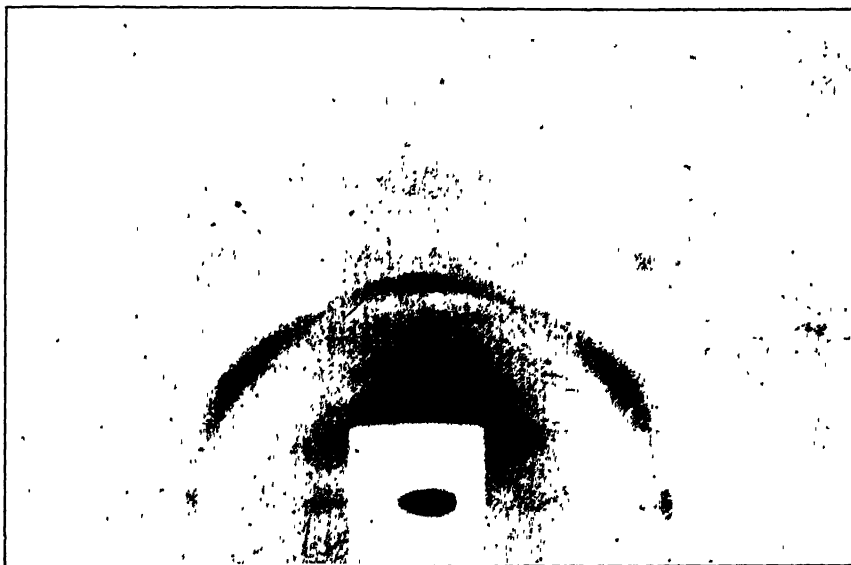


FIG. 21.—DIFFRACTION PATTERN OF COLD-ROLLED ARMCO IRON.

after quenching was examined under the microscope and the old austenite grains were found to be of the same order of magnitude as the ferrite grains that produced the pattern shown in Fig. 22. Each austenite grain must have transformed into many ferrite grains and these must be randomly oriented in order to produce the pattern shown in Fig. 23.

Tungsten, molybdenum, and iron crystallize with body-centered cubic space lattices. Polanyi and Weissenberg have examined severely worked copper and aluminum that crystallize with face-centered cubic lattices and have found directional orientation with mostly one set of 111 planes (easiest slip planes in face-centered lattice) in a cross-section of either wire or foil, but in a small proportion of the section one of the 100 planes (next easiest planes of slip) is parallel to the cross-section.

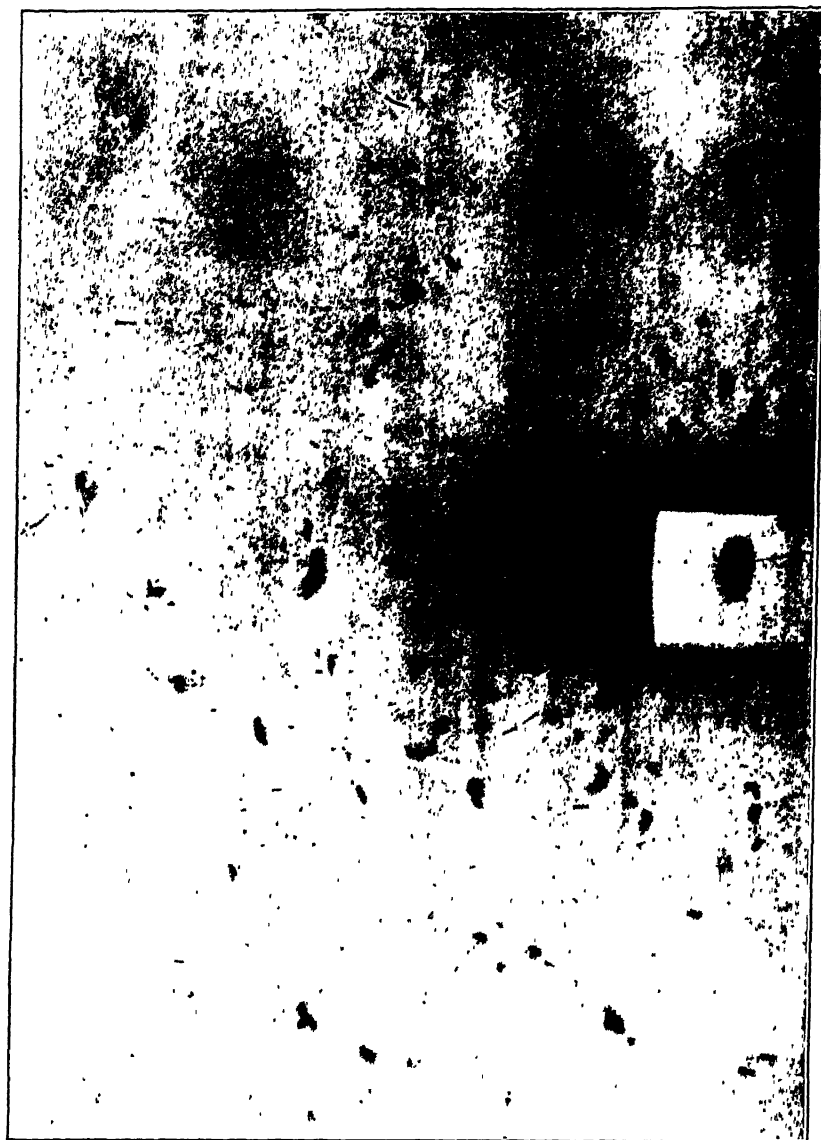


FIG. 22.—DIFFRACTION PATTERN OF ARMCO IRON COLD ROLLED AND ANNEALED AT 950° C.

## GENERAL CONCLUSIONS

From all the results available, certain conclusions can be drawn.

1. The mechanical working of an aggregate of grains with random orientation gradually changes the orientation of the grain fragments produced by slip toward certain definite positions with reference to the direction of working.

2. The definite orientations toward which the grain fragments tend are different in the various types of space lattices.

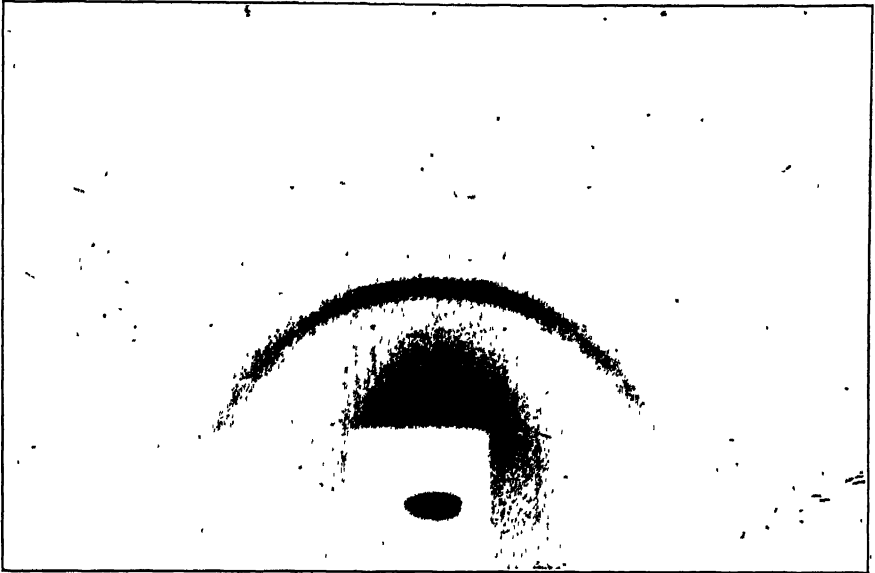


FIG. 23 —DIFFRACTION PATTERN OF 0.3-PER CENT. CARBON STEEL QUENCHED FROM 900° C.

3. Only in extreme cases of mechanical working are substantially all the grain fragments brought into the preferred orientation. In cases of extreme rolling, the structure of a foil approximates that of a single crystal. The structure of a severely drawn wire never approximates that of a single crystal.

4. Due to the tendency toward directional orientation by mechanical work and to the uneven progress of different portions of the section toward preferred orientations, the first working of an aggregate of large grains or of a single crystal that is not initially in the preferred orientation produces a change toward random orientations.

5. The phenomenon of recrystallization is simply the growth of the differently oriented grain fragments produced by plastic deformation.

6. The allotropic transformation in iron at  $A_s$  produces new orientations.

Many other conclusions can be deduced but time does not permit of their consideration. Assuming that the conclusions mentioned are proved or will be modified to fit more exactly future findings, then all facts relating to plastic deformation and to the properties of worked metals must be brought into line with the new conceptions. The elaborate theories that have been put forward to explain the properties of worked metals on the assumption that each grain retains its original orientation during plastic deformation must be put in the discard.

Worked iron and steel can be heated above the upper critical temperature and thoroughly random orientations of the ferrite grains can be produced. One would anticipate the formation of new and random orientations in the  $\alpha \rightleftharpoons \beta$  transformation in brass. Other metals that have been worked any considerable amount and that do not have such transformations in the solid state will retain the effects of working in the crystalline structure whether in the as-worked or the recrystallized condition.

We have known for several years that although wires can be drawn until they show no appreciable general elongation when broken in tension, the reduction of area at the point of fracture is very marked. In the finest tungsten wires, the reduction of area is on the order of 60 per cent. This fact is easily explained on the basis of the new information on the relation between working and crystal structure. Several of the planes of easy slip are disposed, in severely drawn wire, in such a manner as to make the deformation relatively easy in directions necessary for high reduction of area. This is also true of severely rolled sheet.

Many of you may recall the classical work of the late J. E. Stead<sup>17</sup> on "Brittleness Produced in Soft Steel by Annealing." This peculiar brittleness is sometimes referred to as Stead's brittleness. Soft steel sheets after annealing below the critical range in certain cases showed cleavage fracture on three planes perpendicular to one another. One of the planes was parallel with the sheet surface and the other two were perpendicular to the surface and made angles of 45° with the direction of rolling. These are the preferred positions of the cube faces (100) in a body-centered cubic space lattice after severe rolling. The x-ray results, together with Stead's results, demonstrate conclusively that the planes of easiest slip (110) are not the planes of easiest cleavage (100). The cleavage planes are, however, second in ease of slip. Stead's interpretation of this phenomenon was, in general, correct. He states, "We are led from this to conclude that, just as light impresses a latent image on a bromide photographic plate which cannot be seen but is developed and made manifest by the action of certain chemical agencies, so the rolling appears to impress a latent disposition in the steel to crystallize in certain fixed

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<sup>17</sup> Iron and Steel Inst. (1898) II; *The Metallographist* (1899) 2, II, 85.

positions, and annealing develops it afterwards." The degree of directional orientation in the as-rolled sheets is probably much greater than Stead anticipated. It is, however, the deviation from the preferred orientations of many of the grain fragments on a submicroscopic scale that accounts for the absence of cleavage brittleness in the as-rolled sheets.

The metallurgical world practically ignored the lead given by Stead. This was one of the problems that could not be answered definitely with the tools available; perhaps some thought it never could be answered definitely. As is often the case, a majority guessed wrong.

Knowledge increases slowly when each fact has to be found by random hunting; it increases by leaps and bounds as our understanding of fundamentals becomes clearer. By studying grains and crystal fragments with the *x*-ray, we have obtained a better understanding of the fundamentals of the plastic deformation of metals. The determination of the orientation of crystal fragments has been the means of changing our own minds toward proper orientation.

## Some Low Copper-Nickel Silvers

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(New York Meeting, February, 1924)

THIS investigation of low copper-nickel silvers was undertaken to check the work of Léon Guillet on special brasses and to determine, more accurately, the effect of the addition of nickel on the microstructure of the binary alloys of copper and zinc. It was hoped that the results could be successfully applied to the practical production of low copper-nickel silvers.

To explain the results of his investigations on special brasses, Léon Guillet evolved his conception of "fictitious compositions." He states,<sup>1</sup> in his general conclusions, that on the introduction of a small amount of a third metal to a copper-zinc alloy, it enters into solid solution with the normal constituents up to saturation, but by so doing it brings the ternary alloy into a state microscopically equivalent to a binary copper-zinc alloy of fictitious composition, and physically more nearly like the latter than the brass containing copper-zinc in the ratio actually present. The physical properties of the ternary alloy, when compared to the same properties of an actual brass of the fictitious composition, are modified by the natural properties of the third element. Beyond the point of saturation, a special constituent appears and the above generalization no longer holds.

For example, if a 60:40 brass has 4 per cent. of tin substituted for 4 per cent. of zinc, the actual composition would analyze 60:36:4. Assuming that 1 per cent. of tin plays the same part as 2 per cent. of zinc, the proportions of copper and equivalent zinc may be stated as 60 parts of copper and 44 parts of zinc, which, figured to 100 per cent., gives an analysis of 57.7 per cent. of copper and 42.3 per cent. of zinc, the fictitious composition for a 60:36:4 tin brass.

The relation between ternary alloys containing copper and zinc together with a third metal, and the microscopically equivalent binary alloy of copper and zinc, may be expressed mathematically.

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<sup>1</sup> *Rev. de Métallurgie Mem.*, (1905) 97; (1069) 242; (1913) 1130.

When a metal added to a brass possesses a coefficient of equivalence  $t$ , 1 per cent. of this metal will enter into solid solution and replace  $t$  per cent. of zinc, the proportions thus obtained being figured to 100.

Let  $A$  = real percentage of copper;  
 $B$  = real percentage of zinc;  
 $q$  = real percentage of third metal.

Then  $A + B + q = 100$

Let  $A'$  = fictitious percentage of copper;

$B'$  = fictitious percentage of zinc;

and  $t$  = coefficient of equivalence.

Then  $A' + B' = 100$

and  $B' = \frac{B + tq}{A + (B + tq)}$

Solving these equations, we obtain expressions for the values of  $A'$ , the fictitious copper content of a given ternary alloy;  $q$ , the amount of a third metal to be added to a brass in order to produce a ternary alloy structurally similar to any given fictitious brass; and  $t$ , the coefficient of equivalence of a metal of which  $q$  per cent. will structurally change a given brass to correspond to one of a definite fictitious composition.

Then 
$$A' = \frac{100 A}{100 + q(t-1)}$$

$$q = \frac{100}{t-1} \frac{(A - A')}{A'}$$

$$t = 1 + \frac{100}{q} \frac{(A - A')}{A'}$$

These equations are useful in a general way; but as they depend so largely on the accuracy with which we can determine the quantity of zinc replaced by 1 per cent. of any third metal, their value is always open to question until this quantity, the so-called coefficient of equivalence  $t$ , has been firmly established and proved correct.

#### NICKEL BRASSES

From the general results obtained by Léon Guillet, in regard to the effect of the addition of nickel to brasses, and published in the *Revue de Métallurgie* 1913-20 under the title of "The Important Rôle Played by Nickel in the Manufacture of Low-copper Ternary Brasses," it was thought that it would be possible to produce ternary alloys of copper, nickel, and zinc that would possess the valuable hot- and cold-working properties similar to those found in certain commercial binary alloys of copper and zinc.



As the coefficient of equivalence  $t$  for nickel is a negative value, these ternary alloys will contain lower percentages of copper and higher percentages of zinc than are found in the binary copper-zinc alloys showing similar structural and physical properties. This fact, coupled with the natural change in color, increased tensile strength, resistance to corrosion, and improved mechanical properties imparted by the addition of nickel gave promise of alloys worthy of investigation, both because of their microstructures and because of their probable commercial importance and value.

In Table 1 are given some of the results obtained by Léon Guillet in his researches concerning the effect of the addition of nickel to brass, according to which the coefficient of equivalence for nickel is between  $t = -1.1$  and  $-1.4$ .

TABLE 1.—*Data Obtained from Léon Guillet's Study of Nickel Brasses*

	Assay of Alloy		Fictitious Values of Copper Determined by Microscope, Per Cent	Calculated Coefficient of Equivalence, $t$
	Copper, Per Cent.	Nickel, Per Cent		
First series. . . .	55.10	0 59	55.7	-1.1
	55.14	1.02	56 5	-1.4
	55 95	2.03	58 55	-1.2
	55 41	5.02	62 00	-1 1
Second series. . .	49 46	0.50	54 7	-1.1
	49 07	1 00	54 7	-1 1
	49.47	2 02	54 7	-1.1
	49.48	5 02	56.0	-1 3
	49.24	9 81	62.0	-1.1

Substituting these values for the coefficient of equivalence of nickel in the equation  $A' = \frac{100 A}{100 + q(t-1)}$  shows that the accuracy of this equation is only approximate when the values of  $t$  are known only within the limits  $-1.1$  and  $-1.4$ . For example, if the ternary alloys of copper, zinc, and nickel, containing 5 and 18 per cent. of nickel, respectively, which are structurally comparable to a fictitious 60:40 brass, is calculated, using first the lowest value of  $t$  and then the highest, the differences shown in Table 2 will be found.

The difference between the copper content of a 5 per cent. nickel silver, corresponding to the fictitious 60:40 brass, when figured with a coefficient of equivalence  $t = -1.1$  and that found when using the value  $t = -1.4$  is 0.9 per cent. while for an 18 per cent. nickel silver, when calculated in a similar manner, the difference is 3.2 per cent. These differences correspond to a percentage variation, when calculated on a

basis of 100 per cent. of approximately 1.7 and 8.6 per cent., respectively. This variation in copper content, which is small and probably unimportant when calculating the copper content of alloys containing low percentages of nickel, becomes larger and of proportionally greater importance when calculating the amounts of copper contained in the nickel-rich alloys.

TABLE 2.—*Calculated Nickel Brasses Equivalent to a 60:40 Brass Using Values of  $t = -1.1$  and  $-1.4$*

Fictitious Binary Alloy		Coefficient of Equivalence $t$	Equivalent Ternary Alloy			Per Cent. Difference in Copper Content Calculated to 100 Per Cent.
Copper, Per Cent	Zinc, Per Cent		Copper, Per Cent.	Nickel, Per Cent.	Zinc, Per Cent.	
60	40	-1.1	53.7	5 0	41.3	1 7
60	40	-1.4	52.8	5.0	42.2	
60	40	-1.1	37 3	18.0	44 7	8.6
60	40	-1.4	34 1	18 0	47.9	

Before attempting to produce low copper-nickel silvers on a commercial scale, it was of the greatest importance to determine, if possible, a more accurate figure for the coefficient of equivalence of nickel than the values given by Guillet. To obtain this value, it was necessary to cast, roll, anneal, and examine microscopically a large number of ternary copper-nickel-zinc alloys that varied in composition over wide ranges of both copper and nickel. For this purpose three large bars of the following approximate compositions were cast.

BAR NO	COPPER, PER CENT.	NICKEL, PER CENT.	ZINC, PER CENT
1	64	6	30
2	57	13	30
3	50	20	30

These bars were used as base alloys from which samples of varying copper and nickel content might easily be prepared by cutting therefrom portions which were melted with the addition of increasingly larger amounts of zinc, and casting the melt into small ingots suitable for rolling, annealing, and examination. These small ingots, containing nickel in quantities somewhat less than the original base alloys and copper and zinc in progressively decreasing and increasing proportions, respectively, were first analyzed, then rolled (in all cases where the malleability was sufficient to allow of this mechanical treatment), and portions finally brought into a state of at least approximate equilibrium by annealing at 600° and 800° C.

for 3 hr. The annealed samples were quickly withdrawn from the furnace and immediately quenched in cold water. Samples were then cut from the quenched alloys, polished, and etched preparatory to microscopic examination. It was assumed that the time of annealing was of sufficient duration to insure that the structural constituents attained a state of equilibrium before the specimens were withdrawn and quenched. This assumption, while probably somewhat presumptuous, was, we believe, sufficiently accurate for the purpose. At least the annealed samples are comparable with alloys receiving commercial mill anneals and, without doubt, the structural constituents reached a state of equilibrium approximating that which would be obtained by prolonged annealing. Errors, such as inaccurate chemical analyses or the personal factor inherent with micro-examinations, would probably offset any errors due to the attainment of metastable instead of stable equilibrium because of insufficient annealing. Any cases in which the observed microstructure seemed doubtful were checked by repeating both the chemical and the micro-analysis.

When discussing the constituents of a ternary alloy, we must always consider them to be in equilibrium at some definite predetermined temperature. As the temperatures of 600° and 800° C. were used throughout this research, we will begin by considering the structural constituents of the binary copper-zinc alloy when in equilibrium at these two temperatures. The four most interesting binary alloys, when considering the structural constituents of copper-zinc alloys in equilibrium at 600° and 800° C., are those which, at the above temperature, lie on the transition or division lines separating alloys that consist entirely of alpha solid solutions from those containing a mixture of the alpha and beta solid solution, and those that lie on the transition line separating the alpha + beta alloys from those composed entirely of beta solid solution. The four copper-zinc alloys that structurally change from alpha to alpha + beta and from alpha + beta to beta at 600° and 800° C. are:

	COPPER, PER CENT.	ZINC,* PER CENT.		
A . . . . .	64.2	35.8	} 600° C.	{ Alpha to alpha + beta
B . . . . .	56.6	43.4		{ Alpha + beta to beta
C . . . . .	67.3	32.7	} 800° C.	{ Alpha to alpha + beta
D . . . . .	60.9	39.1		{ Alpha + beta to beta

All alloys containing less than 35.8 per cent. of zinc consist entirely of alpha solid solution; those with more than 35.8 per cent. and less than 43.4 per cent. of zinc are composed of a mixture of alpha and beta solid solutions; while those with more than 43.4 per cent. of zinc are composed

\* C. H. Mathewson and Philip Davidson: Metallography of Brass. *Jnl. Am. Inst. of Metals* (1917) 11, 14.

entirely of beta solid solution when in equilibrium at 600° C. The same is true for alloys in equilibrium at 800° C., when containing larger, intermediate, and smaller percentages of zinc than alloys *C* and *D*.

Table 3 shows the copper-nickel-zinc alloys calculated from Léon Guillet's formula, using coefficients of equivalence ranging from -1.1 to -1.4, that should microscopically correspond to these four alloys when in equilibrium at the same temperatures. This table illustrates the influ-

TABLE 3.—*Binary Copper-zinc Alloy and Their Calculated Equivalent Ternary Alloys  $t = -1.1$  to  $-1.4$  Inclusive*

Binary Alloys		Equilibrium Temperature, Degrees C	Coefficient of Equivalence, <i>t</i>	Ternary Alloys									Micro-structure
Copper, Per Cent	Zinc, Per Cent			Copper, Per Cent	Nickel, Per Cent	Zinc, Per Cent	Copper, Per Cent	Nickel, Per Cent	Zinc, per Cent	Copper, Per Cent	Nickel, Per Cent	Zinc, Per Cent	
64.2	35.8	600	-1.1	56.1	6	Diff.	48.0	12	Diff.	39.9	18	Diff.	Alpha
64.2	35.8	600	-1.2	55.7	6	Diff.	47.3	12	Diff.	38.8	18	Diff.	Alpha
64.2	35.8	600	-1.3	55.3	6	Diff.	46.5	12	Diff.	37.6	18	Diff.	Alpha
64.2	35.8	600	-1.4	55.0	6	Diff.	45.7	12	Diff.	36.5	18	Diff.	Alpha
56.6	43.4	600	-1.1	49.5	6	Diff.	42.3	12	Diff.	35.2	18	Diff.	Beta
56.6	43.4	600	-1.2	49.2	6	Diff.	41.7	12	Diff.	34.2	18	Diff.	Beta
56.6	43.4	600	-1.3	48.8	6	Diff.	41.0	12	Diff.	33.2	18	Diff.	Beta
56.6	43.4	600	-1.4	48.5	6	Diff.	40.3	12	Diff.	32.2	18	Diff.	Beta
67.3	32.7	800	-1.1	58.8	6	Diff.	50.3	12	Diff.	41.8	18	Diff.	Alpha
67.3	32.7	800	-1.2	58.5	6	Diff.	49.6	12	Diff.	40.7	18	Diff.	Alpha
67.3	32.7	800	-1.3	58.0	6	Diff.	48.7	12	Diff.	39.4	18	Diff.	Alpha
67.3	32.7	800	-1.4	57.6	6	Diff.	47.9	12	Diff.	38.2	18	Diff.	Alpha
60.9	39.1	800	-1.1	53.3	6	Diff.	45.6	12	Diff.	37.9	18	Diff.	Beta
60.9	39.1	800	-1.2	52.9	6	Diff.	44.8	12	Diff.	36.8	18	Diff.	Beta
60.9	39.1	800	-1.3	52.5	6	Diff.	44.1	12	Diff.	35.7	18	Diff.	Beta
60.9	39.1	800	-1.4	52.1	6	Diff.	43.3	12	Diff.	34.6	18	Diff.	Beta

ence of the coefficient of equivalence  $t$  in the equation  $A' = \frac{100A}{100 + q(t-1)}$  and shows how necessary it is that this factor  $t$  be known within the smallest possible limits. Figs. 1 and 2 show the position of the alpha + beta field when calculated by this equation, using values of  $t = -1.1$  and  $-1.4$ .

### EXPERIMENTAL RESULTS

The results of this investigation, obtained from chemical analysis and microscopic examination of alloys prepared in the manner described, are given in Table 4, and are shown in diagrammatic form in Figs. 3 and 4.

These tabulated results and the diagrams show that the coefficient of equivalence  $t$  varies between the values  $-0.91$  and  $-1.33$ . This is a

TABLE 4.—*Chemical Versus Structural Analysis of Some Low Copper-Nickel Silvers*

Alloy Number	Analysis			Color	Cold Rolled or Cast	Microstructure Equilibrium Temperature		Remarks
	Copper, Per Cent.	Nickel, Per Cent.	Zinc, Per Cent.			600° C.	800° C.	
1	62.11	6.12	Diff.	Pale Gold	Rolled OK	Alpha	Alpha	Only trace of alpha at 600° C.
2	61.18	5.84	Diff.	Pale Gold	Rolled OK	Alpha	Alpha	
3	58.70	5.87	Diff.	Pale Gold	Rolled OK	Alpha	Alpha	
4	57.54	5.79	Diff.	Pale Gold	Rolled OK	Alpha	Alpha + Beta	
5	56.26	5.90	Diff.	Pale Gold	Rolled OK	Alpha + Beta	Alpha + Beta	
6	52.13	5.62	Diff.	Pale Gold	Cast	Alpha + Beta	Beta	
7	50.21	5.85	Diff.	Pale Gold	Cast	Alpha + Beta	Beta	
8	49.67	6.40	Diff.	Pale Gold	Cast	Alpha + Beta	Beta	
9	46.64	5.65	Diff.	Pale Gold	Cast	Beta	Beta	
10	55.75	12.17	Diff.	Yellowish White	Rolled OK	Alpha	Alpha	Only trace of alpha at 600° C.
11	51.03	11.13	Diff.	Yellowish White	Rolled OK	Alpha	Alpha	
12	52.64	11.65	Diff.	Yellowish White	Rolled OK	Alpha	Alpha	
13	50.25	11.46	Diff.	Yellowish White	Rolled OK	Alpha	Alpha + Beta	
14	50.22	11.35	Diff.	Yellowish White	Rolled OK	Alpha + Beta	Alpha + Beta	
15	46.35	11.57	Diff.	Yellowish White	Cast	Alpha + Beta	Beta	
16	44.20	10.84	Diff.	Yellowish White	Cast	Alpha + Beta	Beta	
17	43.77	11.14	Diff.	Yellowish White	Cast	Alpha + Beta	Beta	
18	42.09	11.63	Diff.	Yellowish White	Cast	Alpha + Beta	Beta	
19	41.69	11.50	Diff.	Yellowish White	Cast	Beta	Beta	
20	41.55	11.39	Diff.	Yellowish White	Cast	Beta	Beta	
21	49.11	17.36	Diff.	Silver White	Rolled OK	Alpha	Alpha	Only trace of alpha at 600° C.
22	48.92	17.80	Diff.	Silver White	Rolled OK	Alpha	Alpha	
23	44.02	17.41	Diff.	Silver White	Rolled OK	Alpha	Alpha	
24	42.20	16.20	Diff.	Silver White	Rolled OK	Alpha	Alpha + Beta	
25	42.14	17.19	Diff.	Silver White	Cast	Alpha	Alpha + Beta	
26	41.10	16.70	Diff.	Silver White	Cast	Alpha + Beta	Alpha + Beta	
27	39.80	16.47	Diff.	Silver White	Cast	Alpha + Beta	Alpha + Beta	
28	39.00	16.86	Diff.	Silver White	Cast	Alpha + Beta	Alpha + Beta	
29	38.41	16.35	Diff.	Silver White	Cast	Alpha + Beta	Alpha + Beta	
30	37.88	16.50	Diff.	Silver White	Cast	Alpha + Beta	Alpha + Beta	
31	37.70	16.43	Diff.	Silver White	Cast	Alpha + Beta	Alpha + Beta	
32	37.54	16.37	Diff.	Silver White	Cast	Alpha + Beta	Beta	
33	36.63	15.33	Diff.	Silver White	Cast	Alpha + Beta	Beta	

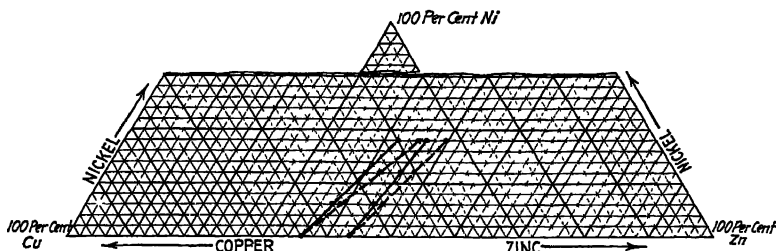


FIG. 1.—CALCULATED BOUNDARY LINES BETWEEN ALPHA, ALPHA + BETA, AND BETA FIELDS FOR Cu-Ni-Zn ALLOYS IN EQUILIBRIUM AT 600° C.; ALPHA + BETA FIELD LIES BETWEEN FULL LINES WHEN CALCULATED BY GUILLET'S FORMULA USING VALUE  $-1.1$  FOR FACTOR  $t$ , AND BETWEEN DOTTED LINES WHEN USING VALUE  $-1.4$  FOR  $t$ .

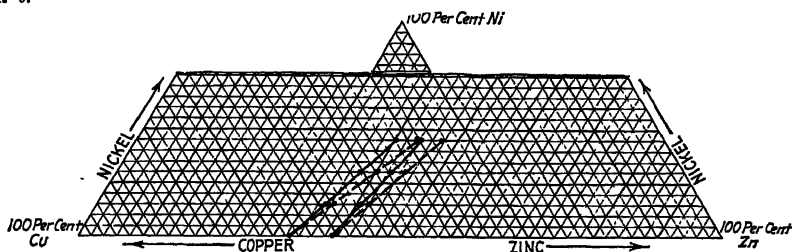


FIG. 2.—CALCULATED BOUNDARY LINES BETWEEN ALPHA, ALPHA + BETA, AND BETA FIELDS FOR Cu-Ni-Zn ALLOYS IN EQUILIBRIUM AT 800° C.; ALPHA + BETA FIELD LIES BETWEEN FULL LINES WHEN CALCULATED FROM GUILLET'S FORMULA USING VALUE  $-1.1$  FOR FACTOR  $t$ , AND BETWEEN DOTTED LINES WHEN USING VALUE  $-1.4$  FOR  $t$ .

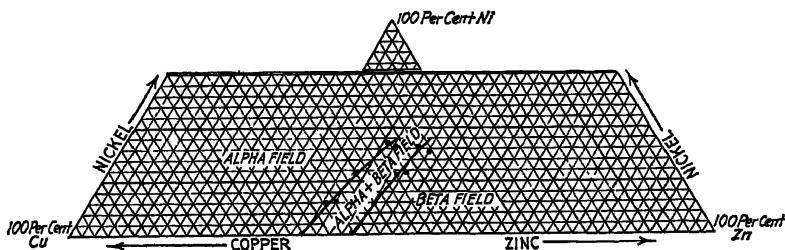


FIG. 3.—BOUNDARY LINES BETWEEN ALPHA, ALPHA + BETA, AND BETA FIELDS PLOTTED FROM CHEMICAL ANALYSIS AND MICRO-EXAMINATION OF SOME LOW-COPPER NICKEL SILVERS IN EQUILIBRIUM AT 600° C.

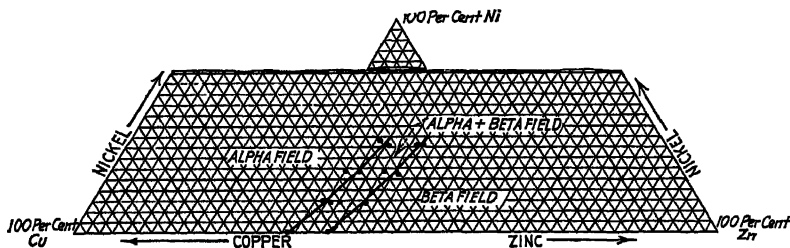


FIG. 4.—BOUNDARY LINES BETWEEN ALPHA, ALPHA + BETA, AND BETA FIELDS PLOTTED FROM CHEMICAL ANALYSIS AND MICRO-EXAMINATION OF SOME LOW-COPPER NICKEL SILVERS IN EQUILIBRIUM AT 800° C.

total variation of 0.42 which is even greater than the variation given by Guillet. However, regardless of these variations, we have concluded, after careful consideration of the variations in chemical analysis of alloys



FIG. 5.—ALLOY No. 3; 600° C.; COPPER 58.7 PER CENT., NICKEL 5.87 PER CENT.; ETCHED WITH  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$  AND  $\text{FeCl}_3$ .  $\times 75$ .



FIG. 6.—ALLOY No. 3; 800° C.; COPPER 58.7 PER CENT., NICKEL 5.87 PER CENT.; ETCHED WITH  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$  AND  $\text{FeCl}_3$ .  $\times 75$ .

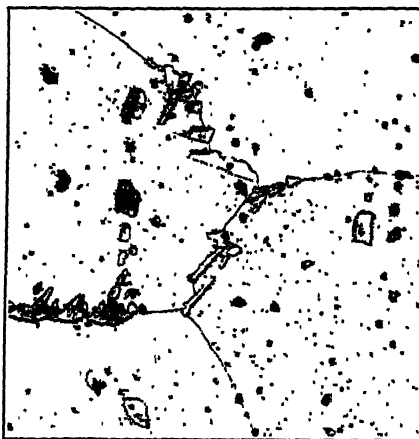


FIG. 7.—ALLOY No. 8; 600° C.; COPPER 49.67 PER CENT., NICKEL 6.4 PER CENT.; ETCHED WITH  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$  AND  $\text{FeCl}_3$ .  $\times 75$ .



FIG. 8.—ALLOY No. 13; 600° C.; COPPER 50.25 PER CENT., NICKEL 11.46 PER CENT.; ETCHED WITH  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$  AND  $\text{FeCl}_3$ .  $\times 75$ .

lying on either side of the boundary lines between the three structural fields and the general appearance of these alloys under the microscope, that the value  $t = -1.1$  is the most accurate figure to use when calculating the fictitious compositions" of all nickel silvers.

The microstructure of some of the alloys made up for this investigation are shown in Figs. 5 to 14. Figs. 5, 8, and 11 show that alloys Nos. 3, 13, and 24 consist entirely of alpha solid solution at 600° C.;

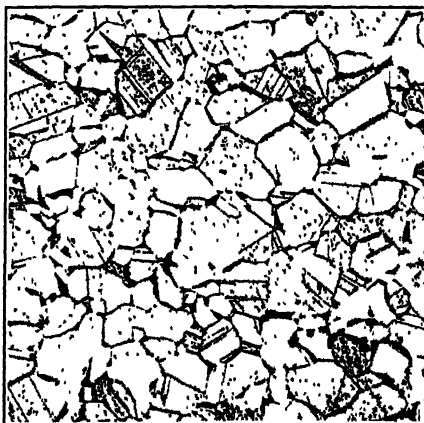


FIG. 9.—ALLOY No. 13; 800° C.; COPPER 50.25 PER CENT., NICKEL 11.46 PER CENT.; ETCHED WITH  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$  AND  $\text{FeCl}_3$ .  $\times 75$ .

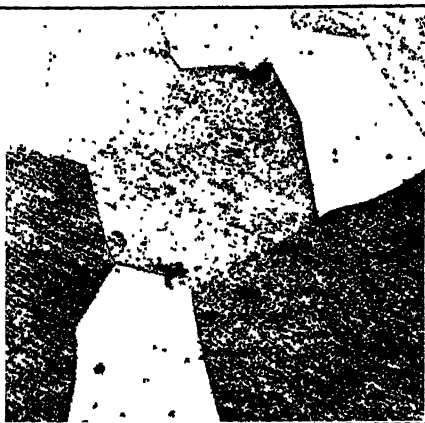


FIG. 10.—ALLOY No. 18; 600° C.; COPPER 42.09 PER CENT., NICKEL 11.63 PER CENT.; ETCHED WITH  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$  AND  $\text{FeCl}_3$ .  $\times 75$ .

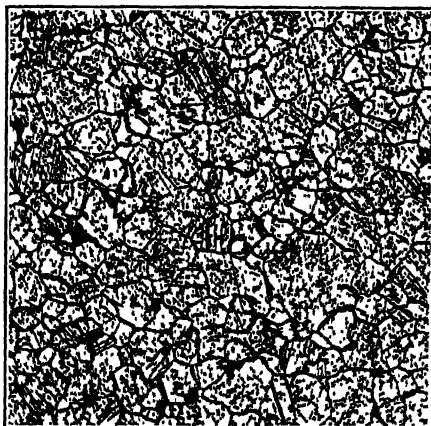


FIG. 11.—ALLOY No. 24; 600° C.; COPPER 43.2 PER CENT., NICKEL 16.2 PER CENT.; ETCHED WITH  $\text{FeCl}_3$ .  $\times 75$ .



FIG. 12.—ALLOY No. 24; 800° C.; COPPER 43.2 PER CENT., NICKEL 16.2 PER CENT.; ETCHED WITH  $\text{FeCl}_3$ .  $\times 75$ .

but Figs. 6, 9, and 12 show that at 800° C. a second constituent is present and that these same alloys are composed of the alpha solid solution plus a small amount of beta solid solution. Alloy No. 8, consisting of beta solid solution plus a trace of alpha, is shown in Fig. 7. Figs. 10 and



14 show alloys Nos. 18 and 33 annealed and quenched at 600° C. These alloys, containing 42.09 per cent. copper, 11.63 per cent. nickel, and 36.63 per cent. copper, 15.33 per cent. nickel, respectively, both consist entirely of beta solid solution. Fig. 13, of alloy No. 27, shows the microstructure of an alloy lying well within the alpha plus beta field when in equilibrium at 600° C. This photomicrograph illustrates a departure from the well-known alpha + beta structure commonly observed, and shows an alloy in which islands of alpha appear scattered throughout a groundmass of beta. Beta is also observed within these islands of alpha.

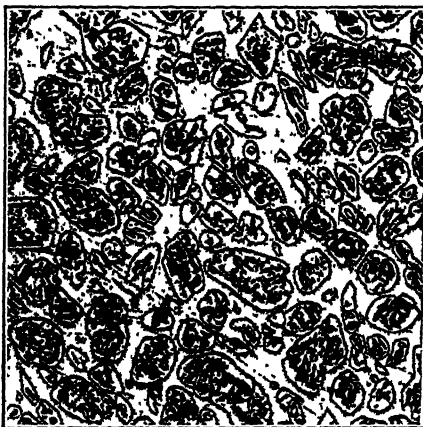


FIG. 13.—ALLOY No. 27; 600° C.; COPPER 39.8 PER CENT., NICKEL 16.47 PER CENT.; ETCHED WITH  $\text{FeCl}_3$ .  $\times 75$ .



FIG. 14.—ALLOY No. 33; 600° C.; COPPER 36.63 PER CENT., NICKEL 15.33 PER CENT., ETCHED WITH  $\text{FeCl}_3$ .  $\times 75$ .

Alloys Nos. 1 to 5, 10 to 14, 21 to 24 inclusive were sufficiently malleable, as cast, to permit of cold rolling; but all others were too brittle and cracked when subjected to this treatment.

The 6 per cent. alloys varied in color from pale gold to a yellowish white; the 12 per cent. alloys were all white with a yellowish cast; while those with higher nickel content varied from a white to a silver white, those with the lowest copper being nearest to silver in appearance.

#### HOT- AND COLD-WORKING ALLOYS

From general observation, it seems that those alloys in which the alpha grains are completely surrounded by an envelope of beta, when hot, and consist, when cold, entirely of alpha or alpha plus the smallest trace of beta are the best alloys for both hot and cold working. Alloys in which there is any great amount of beta present are decidedly brittle and, when subjected to cold working, showed a great tendency to crack.

Those alloys that come within these specifications, that is, structurally consist of alpha plus a slight envelope of beta while hot, but consist almost entirely of the alpha constituent when cold, are listed in Table 5 and diagrammatically represented in Fig. 15.

The best alloys for both hot and cold working lie within a very narrow range. It is, without question, rather hard always to keep within this narrow range when producing these alloys on a commercial scale, but we have fabricated some of these hot- and cold-working alloys on a commercial scale quite successfully. A comparison between the physical properties of two 7 per cent. nickel silvers is shown in Table 6.

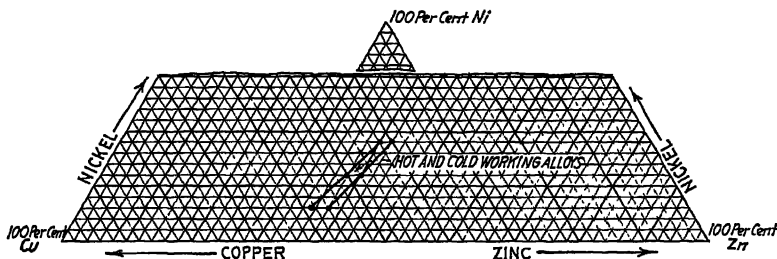


FIG. 15.—ALLOYS SUITABLE FOR HOT AND COLD WORKING. ALLOYS INCLUDED BETWEEN TWO FULL LINES WILL POSSESS BEST HOT- AND COLD-WORKING PROPERTIES; THOSE SLIGHTLY TO RIGHT OF THIS FIELD CAN BE HOT-WORKED BUT ARE LIABLE TO BE HARD AND BRITTLE WHEN COLD; ALLOYS TO LEFT OF THIS FIELD CAN BE COLD-WORKED BUT WILL BE BRITTLE WHILE HOT.

Alloy A is a good cold-working alloy but is unsuitable for hot working; alloy B, with approximately 8 per cent. less copper has the greater ductility and strength. It also has a lower melting point, is of good color, is amenable to both hot and cold working, and is suitable for many purposes for which alloy A is entirely unfit.

TABLE 5—*Compositions of Hot- and Cold-working Nickel Silvers*

PER CENT NICKEL	PER CENT COPPER MINIMUM	PER CENT COPPER MAXIMUM	PER CENT COPPER DESIRED	PER CENT. NICKEL	PER CENT COPPER MINIMUM	PER CENT COPPER MAXIMUM	PER CENT COPPER DESIRED
4	59 00	61.50	60.25	12	48.00	50 20	49.10
5	57 00	60 00	58 50	13	47 00	49 00	48 00
6	56 00	59.00	57 50	14	45.20	47.50	46.20
7	55.00	57 50	56.20	15	44 00	46.00	45.00
8	53.50	56.00	54 20	16	42.50	44.50	43.50
9	52.00	54.50	53 20	17	41.00	43.00	42.00
10	51.00	53.00	52 00	18	40.00	42.00	41.00
11	49 50	51.50	50.00				

### CONCLUSIONS

The best value for the coefficient of equivalence  $t$  to be used in calculating the fictitious compositions of binary copper- zinc alloys structur-

TABLE 6.—*Comparison between Physical Properties of Two 7 Per Cent. Nickel Silvers, One of Which Is a Good Commercial Hot- and Cold-working Alloy*

Alloy Number	Per Cent Copper	Per Cent Lead	Per Cent Iron	Per Cent Nickel	Per Cent Manganese	Per Cent Zinc	Annealed Degrees C	Yield Point Pounds per Square Inch	Tensile Strength Pounds per Square Inch	Per Cent Elongation in 2 in	Per Cent Reduction of Area	Brinell Depth in millimeters	Scleroscope Hardness, Universal Hammer
A	64.68 Cold-working Alloy	Trace	0.104	6.73	0.06	Remainder	Hard Rolled	90,167	90,167	3.5	29.5	3.33	42
								77,550	81,850	6.8	31.5	4.98	40
								44,900	67,000	41.2	40.0	10.01	22
								40,133	64,267	46.2	51.0	10.33	19
								28,367	57,733	57.0	51.7	11.66	15
B	55.85 Hot- and Cold-working Alloy	Less than 0.1	0.094	7.36	none	Remainder	Hard Rolled	22,567	53,833	61.5	56.1	12.19	12
								21,033	49,933	62.3	53.5	12.75	10
								19,800	48,333	62.0	53.6	12.60	10
								98,500	98,500	2.5	18.3	5.67	11
								90,800	93,400	7.0	27.8	5.11	10
								43,900	72,700	14.2	42.3	8.84	27
								34,100	63,100	52.8	40.8	10.72	17
								22,900	57,300	69.3	53.9	11.75	13
								19,600	53,500	75.7	52.8	12.45	11
								17,400	50,800	66.3	45.3	12.55	10
								19,700	52,700	56.3	42.0	12.20	10

Alloy A, cold-working alloy  
Alloy B, hot- and cold-working alloy

Alloy A was tested on 0.050-in gage  
Alloy B was tested on 0.032-in gage

ally and physically similar to any given ternary copper-nickel-zinc alloy is -1.1.

Low copper-nickel silver can be made ranging in color from a pale gold to a yellow white to a silver white, depending on the amount of copper and nickel present.

Alloys can be produced having good hot- and cold-working properties, but these alloys lie within a very narrow range and great care must be taken to keep the composition within this specified zone. The color of these alloys compares favorably with the color of the standard cold-working nickel silvers now on the market. Some of these alloys also have the added advantage of greater ductility and tensile strength.

## Effect of Severe Cold Working on Scratch and Brinell Hardness\*

BY HENRY S. RAWDON† AND WILLARD H. MUTCHLER,‡ WASHINGTON, D. C.

(New York Meeting, February, 1924)

AS PART of the study of the scratch-hardness method for metals and alloys in coöperation with one of the technical committees of the American Society for Testing Materials, the authors devoted considerable time to the study of the changes in hardness of metals when cold rolled. Various seemingly contradictory statements in the technical literature concerning the applicability of the scratch-hardness method to such cold-rolled materials were among the principal reasons for the investigation, the results of which are in part presented here. The effect of cold deformation, at least in moderate degrees, on the hardness as measured by the Brinell and other common methods is so well known that further reference is unnecessary.

Concerning the scratch hardness of cold-worked metals, Martens and Heyn state<sup>1</sup> that hardness, whether measured by the ball-pressure method (Kugeldruck) or by the scratch method (Ritzverfahren), will be increased by cold deformation. Jeffries and Archer give a seemingly diametrically opposite view. They state,<sup>2</sup> that "the sclerometer (indicating scratch hardness) shows little difference between cold-worked and annealed metals." Portevin<sup>3</sup> has shown that the rate at which the Brinell hardness of cold-worked copper and brass increases is very high for relatively slight deformation after which it drops to zero, while Merica and Waltenberg<sup>4</sup> have observed that monel metal shows evidence of softening on

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† Physicist, Bureau of Standards.

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<sup>1</sup> Martens-Heyn: *Materialienkunde für den Maschinenbau*, II A, 260.

<sup>2</sup> Jeffries and Archer: *The Properties of Cold-Worked Metals: Chem. & Met. Eng.* (1922) 27, 880.

<sup>3</sup> A. Portevin: *La dureté à la bille du cuivre et des laitons écrouis. Rev. de Met.* (1919) 16, 235.

<sup>4</sup> Unpublished work on monel metal carried out at the Bureau of Standards by a representative of the International Nickel Co.

severe cold working. Other statements might be quoted,<sup>5</sup> showing the anomalous changes in the properties of metals on cold working. The authors believe that the results presented here will help reconcile the seemingly contradictory statements just quoted.

### METHOD AND MATERIALS

The method employed in this study consisted of the cold rolling of various annealed metals without any intermediate annealing and the determination of the hardness at various stages of the rolling. The rate of deformation was regulated as carefully as was possible with the small hand-operated rolls used, and the rolling was continued as far as the apparatus would permit, without resorting to the device of rolling several sheets in one operation. The results summarized in Table 1 are typical of the rolling conditions of the various metals used. After the reduction of the strip to an approximate thickness previously decided on, a portion was sheared off and saved for hardness determinations and the rolling continued until the strip was reduced sufficiently for the next specimen; and so on. In the case of the very soft metals, tin, aluminum, and zinc, the hardness was determined immediately after rolling so as to obviate any possible "self-annealing" effect.

The hardness was determined by means of the scratch method, the instrument described by C. H. Bierbaum<sup>6</sup> being used. The width of the cut produced was measured at a magnification of approximately 500 diameters. Hardness determinations by the Brinell method were also made. A "dead-weight" instrument that employs a 1.59-mm. ( $\frac{1}{16}$ -in.) ball and 6.4-kg. load was used<sup>7</sup> for this purpose.

To show the permanence of the effect produced in the metal by cold deformation, specimens of copper rolled to different thicknesses were annealed at 100° C. for different lengths of time, after which the hardness was redetermined. Likewise a set of the cold-rolled copper strips was fully annealed (450° C.) and the hardness then determined in order to check out the possible effect that the thinness of the specimen might have on the results of the hardness tests.

### RESULTS

The results summarized in Table 1 for annealed commercial cast copper and represented graphically in Fig. 1 are typical of the results obtained

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<sup>5</sup> See, for example, W. E. Atkins: *The Effect of Progressive Cold Drawing upon Some Physical Properties of Commercially Pure Copper*. *Jnl. Inst. of Metals* (1920) 23, 381.

<sup>6</sup> C. H. Bierbaum: *A Study of Bearing Metals*. *Trans.* (1923) 69, 972.

<sup>7</sup> H. S. Rawdon and E. Jimeno-Gill: *Bur. of Stand. Sci. Paper* 397.

for all the metals used. A marked increase in hardness, as measured by the Brinell and the scratch methods, during the initial stages of deformation was noted in all cases. The behavior of the metal in this regard

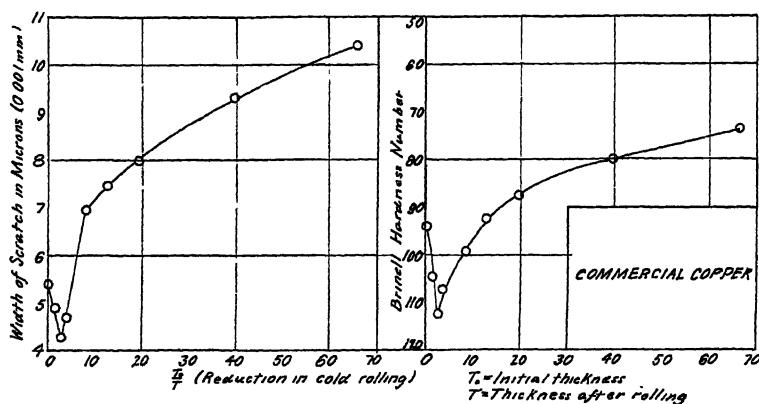


FIG. 1.—EFFECT OF SEVERE COLD ROLLING ON HARDNESS OF COMMERCIAL COPPER.

does not continue, however, throughout the process of deformation; a maximum hardness is reached and a reversal occurs, the specimen becoming softer as the cold working is continued. After one becomes accustomed to the “feel” of the metal in operating the rolls, the changes in the

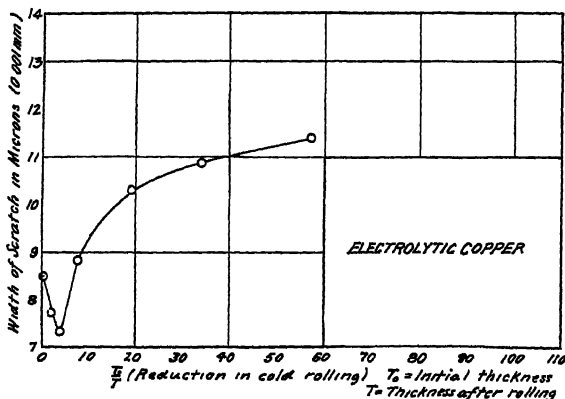


FIG. 2.—RELATION OF SCRATCH HARDNESS OF ELECTROLYTIC COPPER (UNMELTED) TO AMOUNT OF COLD ROLLING RECEIVED.

hardness can be readily noted. If any cracking or splitting occurs, it will take place during the stages of deformation represented by the descending branch of the curve, usually near the minimum; that is, at the time of greatest hardness. The deformation corresponding to the second or

ascending branch of the curve can be carried out much more easily and with much less chance of damaging the strip by cracks or splits than can the initial deformation.

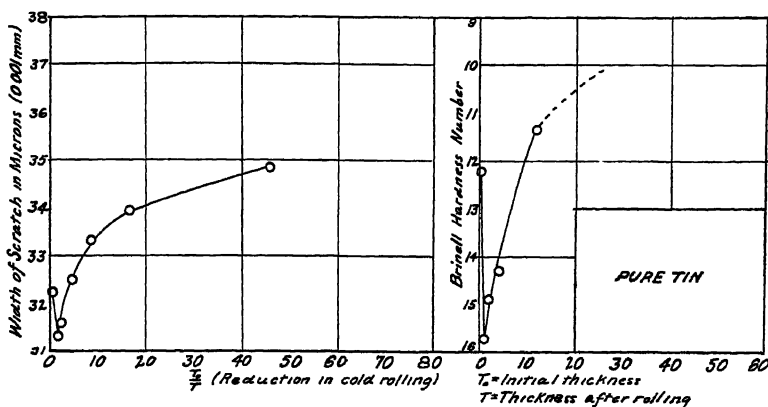


FIG. 3.—HARDNESS CHANGES PRODUCED IN VERY PURE TIN BY SEVERE COLD ROLLING.

The following materials were cold rolled in the manner indicated: commercial cast copper (annealed), electrolytic copper (unmelted), electrolytic iron (vacuum fused), 0.21-per cent. carbon steel, aluminum (99.9 per cent.), commercial aluminum, zinc (99.98 per cent.), Benedict

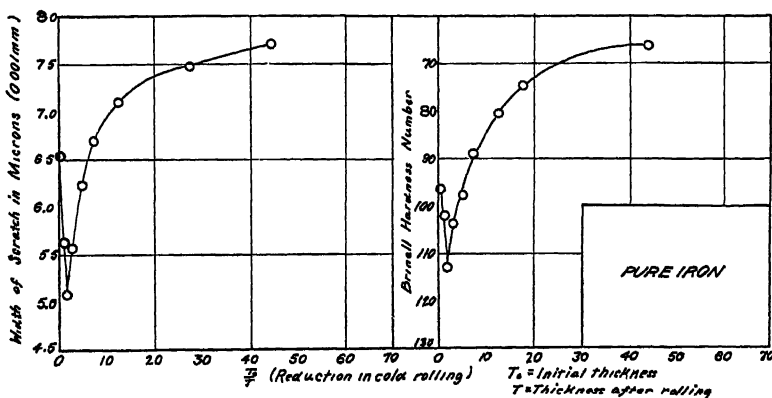


FIG. 4.—HARDNESS CHANGES PRODUCED IN ELECTROLYTIC IRON, VACUUM FUSED, BY SEVERE COLD ROLLING.

metal (nickel 20 per cent., copper 80 per cent.), tin (99.997 per cent.). The general form of the curve showing the relation between deformation and resulting hardness was the same in each case, as shown in Figs. 1 to 6.



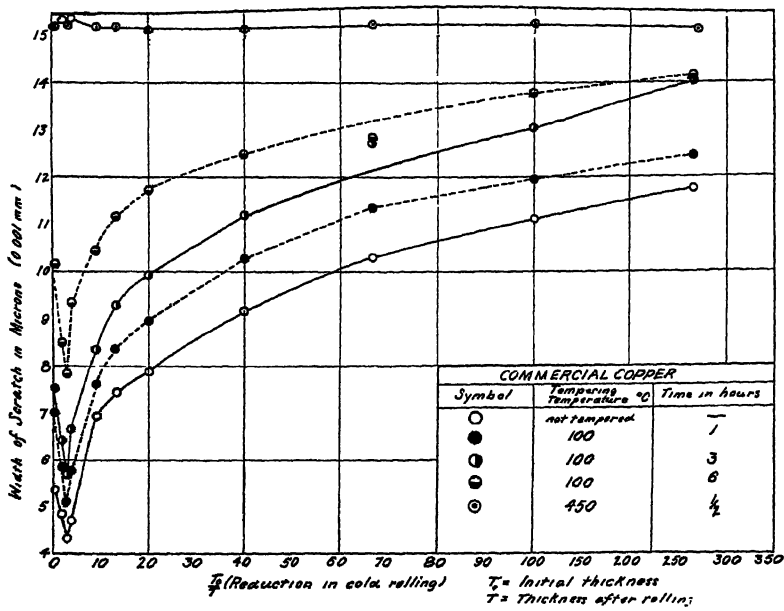


FIG. 5(a).—EFFECT OF ANNEALING ON SCRATCH HARDNESS OF COMMERCIAL COPPER PREVIOUSLY COLD ROLLED, AS IN FIG. 1.

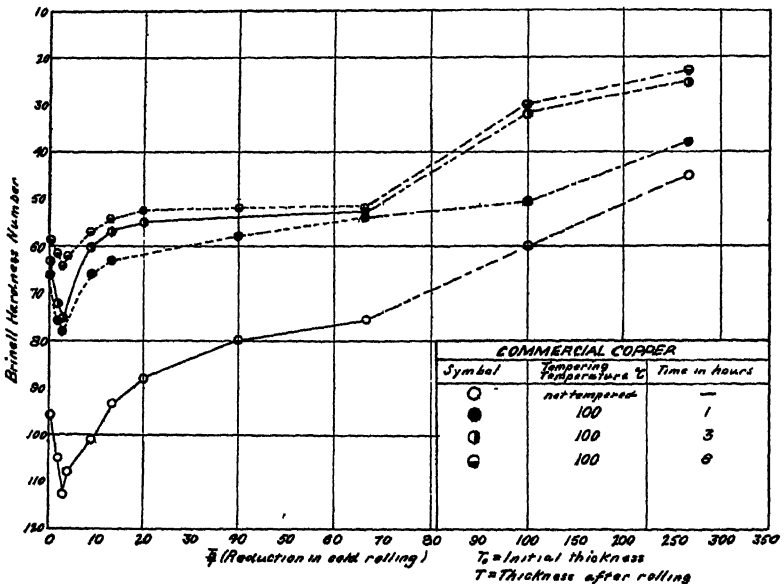


FIG. 5(b).—EFFECT OF ANNEALING ON BRINELL HARDNESS OF COMMERCIAL COPPER PREVIOUSLY COLD ROLLED, AS IN FIG. 1.

In the case of the softer metals, zinc, aluminum, and tin, most of the hardness tests were taken immediately after rolling in order to avoid any possible change resulting from "self annealing." The results summarized

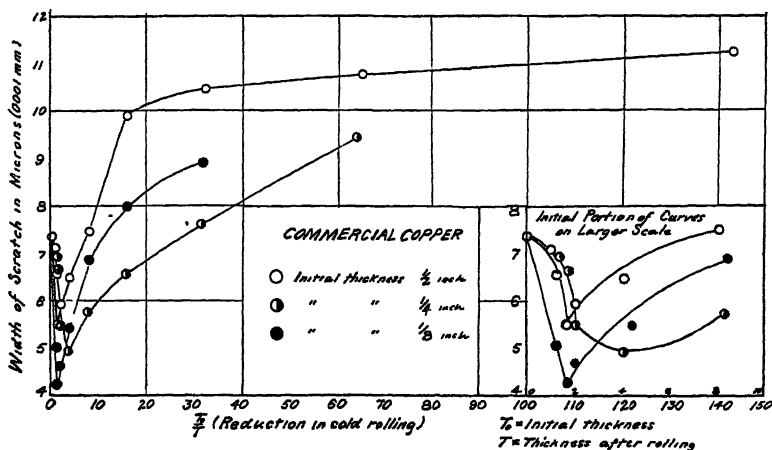


FIG. 6(a).—SCRATCH HARDNESS CHANGES IN COMMERCIAL COPPER RESULTING ON COLD ROLLING ANNEALED SPECIMENS VARYING IN THEIR INITIAL THICKNESS.

below, showing the changes produced in cold-rolled copper by low-temperature annealing, indicate that self-annealing if it did occur would not change the general form of the hardness curve, at least for a considerable length of time.

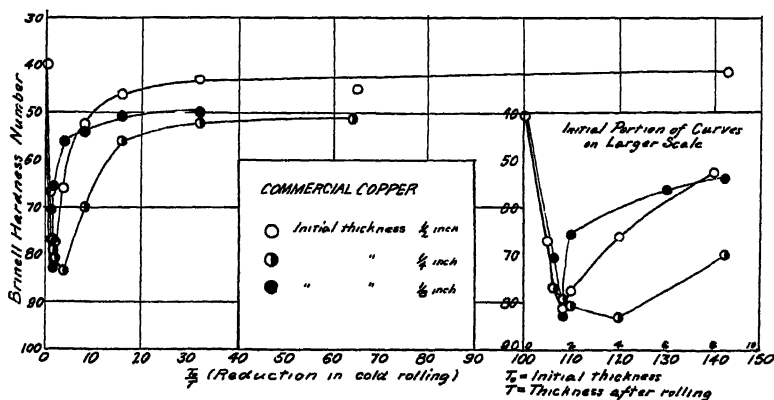


FIG 6(b).—BRINELL-HARDNESS CHANGES IN COMMERCIAL COPPER RESULTING ON COLD ROLLING ANNEALED SPECIMENS VARYING IN THEIR INITIAL THICKNESS.

The effect of low-temperature annealing on the hardness of cold-rolled strips of commercial copper is shown in Fig. 5(a) and (b). The specimens were annealed (100° C.) in an electrically heated laboratory oven.

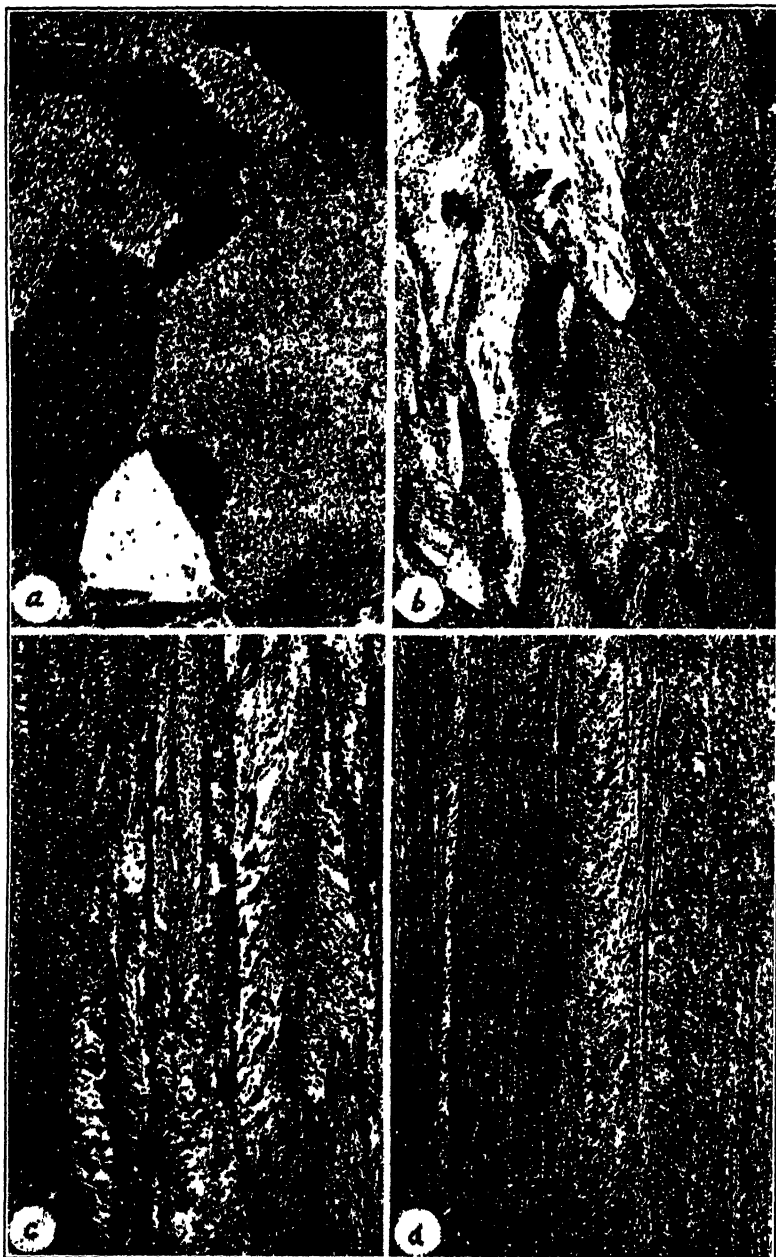


FIG. 7.—MICROSTRUCTURAL CHANGES INDUCED IN ELECTROLYTIC COPPER BY VARIOUS DEGREES OF COLD ROLLING.  $\times 500$ .

(a) INITIAL CONDITION, 0.157 IN. THICK ANNEALED; (b) COLD-ROLLED, DEFORMATION RATIO  $\left(\frac{T_0}{T}\right)$  2.1; (c) COLD-ROLLED,  $\frac{T_0}{T} = 4.1$ ; (d) COLD-ROLLED,  $\frac{T_0}{T} = 8.3$ .

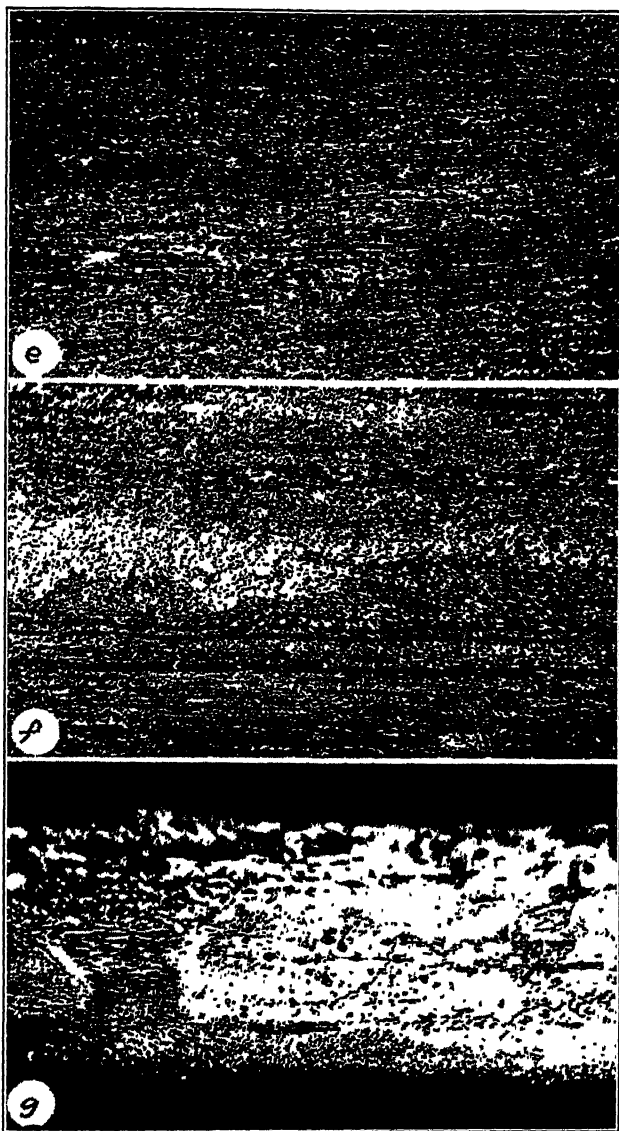


FIG. 7. *Continued.*—MICROSTRUCTURAL CHANGES INDUCED IN ELECTROLYTIC COPPER BY VARIOUS DEGREES OF COLD ROLLING.  $\times 500$ .

[(e) COLD-ROLLED,  $\frac{T_0}{T} = 14.3$ ; (f) COLD-ROLLED,  $\frac{T_0}{T} = 22.4$ ; (g) COLD ROLLED,  $\frac{T_0}{T} = 52.3$ . ETCHING REAGENT THROUGHOUT, AMMONIUM HYDROXIDE AND HYDROGEN PEROXIDE.

Although the copper became materially softer on annealing, the differences in hardness between the strips that had received different degrees of cold working were pronounced even after 6 hr. heating at 100° C. After heating all the specimens of one rolling of commercial copper for 30 min. at 450° C., it was found that all had the same scratch hardness, thus demonstrating that the hardness differences noted for the cold-rolled strips represented real differences in the metal and not a mere consequence of the increasing thinness of the strips.

In Fig. 6(a) and (b) are given the results obtained by cold rolling three strips of the same material (commercial copper) that differed materially in their initial thickness. Strips of  $\frac{1}{2}$ ,  $\frac{1}{4}$ , and  $\frac{1}{8}$  in. initial thickness were used. The results show that two rolled specimens having the same deformation ratio  $\frac{T_0}{T}$  are not necessarily of the same hardness.

As might be predicted, the initially thinner specimens harden more rapidly, that is at the lower deformation ratios, than do thicker ones, for the same pass reduction.

In Fig. 7 are shown the changes in microstructure which result from cold rolling electrolytic copper without any intervening annealing during the process. The curves showing the accompanying hardness changes of this material are given in Fig. 2. The photomicrographs show that softening of the metal by severe deformation does not occur until all evidence of the crystal structure has been destroyed. Deformation of the crystals with the characteristic "slipping" in the interior of the grain accompanies the hardening of the metal during the initial stages of cold-rolling. By the time the metal attains its maximum hardness, the crystalline structure has been very much distorted and further rolling gives rise to structure having a uniform fibrous appearance, as seen in longitudinal sections perpendicular to the rolled surface. The true shape of the deformed grains is that of extremely thin flat scales.

## DISCUSSION

The results obtained in this investigation explain satisfactorily the seemingly contradictory statements that have been made concerning the scratch hardness of cold-rolled metals. Inasmuch as the degree of cold rolling is not usually mentioned, it is not surprising, in the light of the real nature of the effect produced by cold rolling, that such statements have been made. Evidently most generalizations concerning the hardening effect of cold deformation and the method by which this effect is brought about have been based on results obtained with metals subjected to relatively low degrees of working, that is to the descending branch of the complete curve.

The authors are not attempting any explanation of the underlying cause of the reversal in the hardening process of metals on severe cold

deformation. Any theory that might be advanced demands more substantiating experimental evidence than the investigation, in its present stage, affords. Experiments on the severely worked metals involving the

TABLE 1.—*Progressive Cold Rolling of Commercial Copper*

Specimen Number	Thickness, Inch	Reduction in Thickness by Cold Work, Inch	Reduction Ratio, <sup>a</sup> $\frac{T_0}{T}$	Number of Passes through Rolls to Effect Reduction <sup>b</sup>	Hardness			
					Brinell Hardness Number	Width of Scratch, in Microns <sup>c</sup>		
						Longitudinal	Transverse	Average
1	0 400	0 0	0	0	95.5			5 36
2	0 212	0 188	1 89	21	104 8	4 67	5 20	4 93
3	0 134	0 078	2 98	18	112.4	4 34	4 29	4 32
4	0 096	0.038	4 17	15	107 8	4.71	4.72	4 71
5	0 045	0 051	8 9	11	100 9	6 92	6 94	6.93
6	0 030	0 015	13 3	6	93 3	7 41	7.46	7 43
7	0 020	0 010	20 0	5	88 0	7.94	7 86	7 90
8	0 010	0 010	40.0	5	80 0	9 22	9 02	9 12
9	0 006	0 004	66 7	2	74 7	10 26	10 34	10 30
10	0.004	0 002	100 0	2	60 <sup>d</sup>	11 16	11 07	11 11
11	0 0015	0 0025	266 0	2	45 <sup>d</sup>	11.71	11.81	11 75

<sup>a</sup>  $T_0$ , initial thickness;  $T$ , thickness of cold-rolled strip.

<sup>b</sup> The roll setting was changed after each pass

<sup>c</sup> 1 micron = 0.001 mm.

<sup>d</sup> Very approximate, because of thinness of strip

TABLE 2.—*Effect of Low-temperature Annealing on Hardness of Severely Cold-rolled Copper*

Specimen Number <sup>a</sup>	Thickness, Inch	Hardness after Annealing at 100° C.						Scratch Hardness after Annealing 450° C 30 min, Microns
		1 Hour		3 Hours		6 Hours		
		Brinell Hardness Number	Scratch, Microns	Brinell Hardness Number	Scratch, Microns	Brinell Hardness Number	Scratch, Microns	
1	0 400	66 0	7 01	63 0	7 53	58 5	10.19	15 20
2	0 212	75 5	5.84	72 0	6 41	61 0	8 50	15 03
3	0 134	78 0	5 11	75 0	5.70	64 0	7 86	15.22
4	0 096	68 0	5 77	71 0	6 69	62 0	9 32	15 35
5	0 045	66.0	7 63	60.0	8.34	57 0	10 46	15 19
6	0 030	63 0	8.38	57.0	9.30	54 0	11 18	15 20
7	0 020	55 5	8 97	55.0	9.92	52 5	12 22	15.15
8	0 010	58 0	10 27	65.0	11 22	...	12 48	15.13
9	0 006	54.0	11 35	52 5	12.72	52 0	12 83	15.21
10	0.004	50 5	11 96	32 0	13 06	...	13.79	15 20
11	0 0015	.	12.45	. .	14 04	..	14 06	15 17

<sup>a</sup> Specimens listed in Table 1 were used.

determination of density and the atomic changes, as revealed by the x-ray crystallographic methods, are in progress; it is hoped that these will throw some light on this subject. Additional work on rolling is also

planned. This will include a study of the hardness of the interior of the cold-rolled strips, that is, as measured on sections perpendicular to the surface in addition to the "surface hardness." The possible effect of the temperature of the strip while being rolled will also receive attention.

### SUMMARY

1. The hardness changes that occur in metals as they are progressively cold rolled were measured by means of the small Brinell testing set and by the scratch-hardness method.

2. During the initial stages of rolling, the metal hardens rapidly. A maximum in hardness is reached, however, at a relatively low-deformation ratio (initial thickness to final thickness) and a reversal occurs, the metal becoming softer as the deformation is continued. In most cases, the severely cold-rolled sheet was softer than the metal in its initial condition.

3. All the metals used gave the same general form of hardness-deformation curve.

4. Annealing the cold-rolled strips at a low temperature (100° C.) softened all of them appreciably. The general form of the hardness-deformation curve was still maintained, however.

5. All the cold-rolled strips of any series, after full annealing, gave the same scratch hardness, thus showing that the test results were independent of the thinness of the strips.

6. During the hardening period in continuous cold working, deformation of the crystals by slipping occurs. In the severely cold-rolled specimens that showed appreciable softening, all evidence of the previously existing crystalline condition had been destroyed.

### DISCUSSION

W. H. BASSETT, Waterbury, Conn. (written discussion).—A study of the paper shows that the authors' results are at variance with the general experience in the cold rolling of copper and copper alloys. It is common rolling-mill experience that the non-ferrous metals and alloys increase in hardness and tensile strength, and decrease in ductility up to a deformation ratio ( $\frac{T_0}{T}$ , Rawdon and Mutchler, nomenclature) of  $4\frac{1}{2}$  to

5. The rates of hardness changes for given amounts of reduction by rolling, or drawing, following a given heat treatment have been so thoroughly worked out that the physical properties of the materials can be practiced within reasonably close limits. The general experience follows that of the authors as to rapidly increasing hardness with slight deformation, the increase progressing more slowly with still further

deformation, but no point has been known at which a reversal takes place. Contrary to the authors' findings, the hardness and tensile strength continue to increase with greater deformation, the rate approaching zero as a limit.

After we received this paper, we cold rolled annealed commercial copper from  $1\frac{1}{4}$  to 0.006 in., measuring the hardness by means of Brinell, Rockwell, and scleroscope tests. The results are given in Table 3 and are plotted in Fig. 8, in comparison with those in Table 1.

TABLE 3.—*Progressive Cold Rolling of Commercial Copper<sup>a</sup>*

Thickness, Inch	Reduction Ratio <sup>c</sup> $\frac{T_0}{T}$	Number of Passes through Rolls to Effect Reduction <sup>d</sup>	Rockwell Hardness			Sclero- scope	Brinell Hardness, 500 Kg Weight, 10-mm Ball
			100 Kg Weight, $\frac{1}{16}$ -in. Ball	60 Kg. Weight, $\frac{1}{8}$ -in. Ball	100 Kg Weight, $\frac{1}{8}$ -in. Ball		
1 25 <sup>b</sup>	0		-10 5	-18	-59	10 0	44 9
0.632	1.98	5	+56 0	+10 9	- 6.5	37 5	107
0 363	3 44	3	63.9	11 9	- 3 0	40 5	114
0 212	5.90	2	64.8	12 9	- 0.5	42 0	117
0 140	8.93	1	69 8	13 7	+ 1 0	43 5	122
0 090	13.9	2	70.5	14.1	+ 1.5	47 5	123
0 059	21 2	2	70.5	14.0	0	48 5	124
0 039	32 1	2	72.5	13 9	0	49.0	122
0 032	39 1	1	72.6	14 1	- 0.5	49 5	
0 026	48 1	1	72 6	14 1	+ 0.5	48 5	
0 022	56 8	1	72 6	14 6	1 3	47 0	
0 018	69 5	1	72 4	14 4	2 0	47 0	
0.013	96 2	2	69.7	14 8	2 8	47 0	
0 009	139	3	43 6	15 8	3 5	48.5	
0 007	179	2	60 4	15 9	- 2 0	49 5	
0 006	217.	6	73	13 9	- 5 5	52 5	

<sup>a</sup> Copper + silver 99.953 per cent.

<sup>b</sup> Hot rolled from 4 to 1.25 in. and allowed to cool from red heat.

<sup>c</sup>  $T_0$ , initial thickness;  $T$ , thickness of cold-rolled strip.

<sup>d</sup> Rolls of 20 in. diam.; copper cooled at each sampling point; copper sawed to 5 in. wide strip at  $1\frac{1}{4}$  in.; but widened to  $5\frac{3}{4}$  in. at 0.0006 in.

These results show an increase in hardness; but no softening is indicated save in those cases where the method of testing was unsuitable because of the thinness of the metal. The authors' curve, on the other hand, shows an increase in hardness up to a reduction ratio ( $\frac{T_0}{T}$ ) of 2.98, and then drops very rapidly. We note that the authors started this experiment with copper that had a Brinell hardness of 95.5, which, from our tables and their own data, indicates that their original bar was hard (approximately 29 per cent. reduction or  $\frac{T_0}{T} = 1.5$ ).



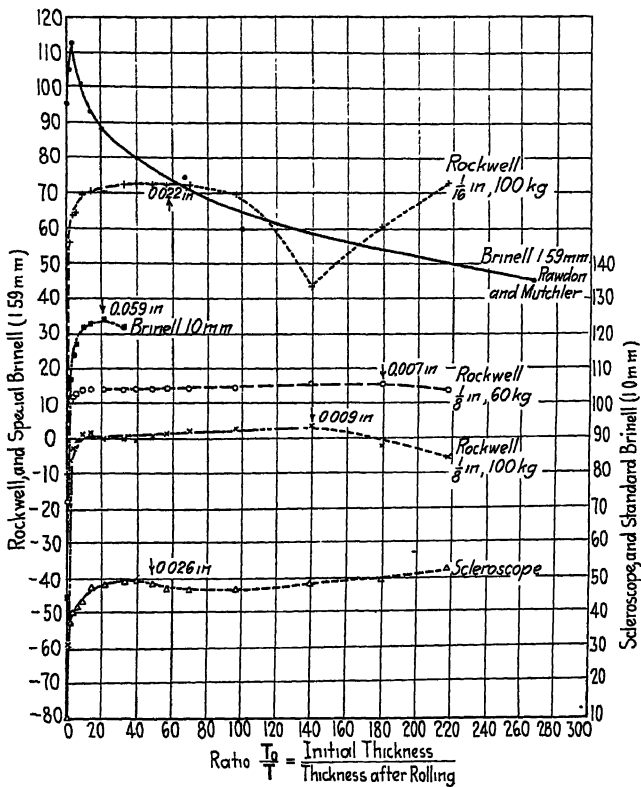


FIG. 8.—COMPARISON OF HARDNESS TESTS ON SEVERELY COLD-WORKED COMMERCIAL COPPER.

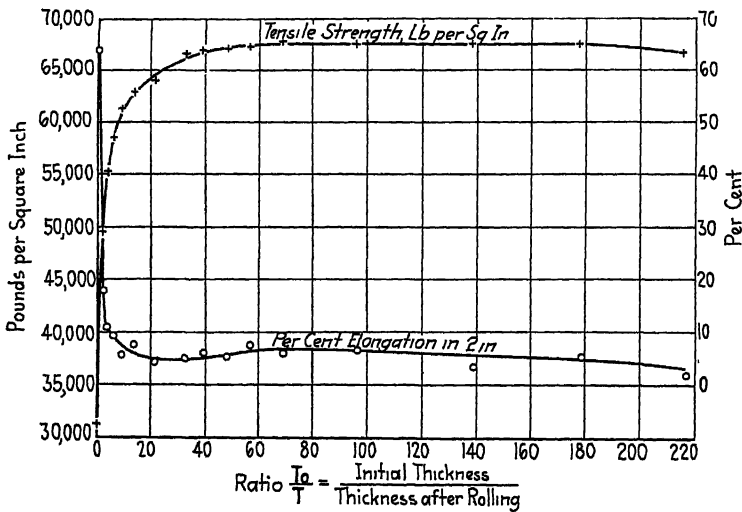


FIG. 9.—COLD ROLLING OF COMMERCIAL COPPER FROM 1.250 IN. TO 0.006 IN.

As no scratch-hardness apparatus was available, we tested by the following methods, which if not entirely standard are, at least, comparative in a single series of samples. The standard Brinell hardness test (500-kg., 10-mm. ball) is not practical for testing hard copper thinner than 0.060 in., therefore our results have not been plotted farther than this gage. The Rockwell test, using a 100-kg. weight and a  $\frac{1}{16}$ -in. ball shows erratic results on hard copper thinner than 0.022-in. With a 60-kg. weight and with a  $\frac{1}{8}$ -in. ball, the test shows erratic results on

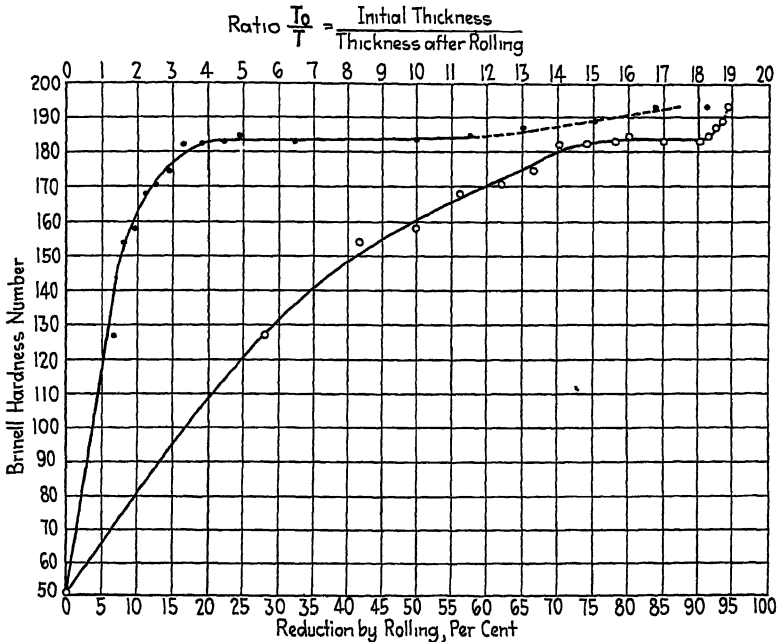


FIG. 10.—COMPARISON OF METHODS OF PLOTTING BRINELL HARDNESS OF BRASS. UPPER CURVE IS  $\frac{T_0}{T} = \frac{\text{INITIAL THICKNESS}}{\text{THICKNESS AFTER ROLLING}}$ ; LOWER CURVE IS  $\frac{T_0 - T}{T_0} \times 100 =$  PER CENT. REDUCTION BY ROLLING.

hard copper thinner than 0.007 in. The Rockwell test, using a 100-kg. weight and a  $\frac{1}{8}$ -in. ball, gives poor results on hard copper thinner than 0.009 in. The scleroscope (vertical type, magnifier hammer) begins to show the effect of the thinness of the copper at about 0.026 in.

The results of tensile strength and elongation data on the same cold-rolled copper series are given in Fig. 9 and Table 4.

Tests upon cold-rolled brass show a progressive increase in hardness similar to that of copper; the data on brass, Table 5, are plotted in Fig. 10.

The hardness curves that we have presented closely resemble those made by A. Portevin<sup>a</sup> whose plotted data are carried to a maximum

<sup>a</sup> A. Portevin: *Rev. de Met.* (1919) 16, 235.

TABLE 4.—*Progressive Cold Rolling of Commercial Copper*

Thickness, Inch	Tensile Strength, <sup>a</sup> Lb per Sq In.	Elongation, <sup>a</sup> Per Cent		Reduction Ratio $\frac{T_0}{T}$
		in 2 in	in 8 in.	
1.25	31,200	64 0	40 4	0
0.632	49,650	18 0	4 94	1 98
0.363	55,450	11 0	3 26	3 44
0.212	58,550	9 5	2 88	5 90
0.140	61,300	5 8	1 75	8 93
0.090	63,050	7 5	2 78	13 9
0.059	64,100	4 5	1 44	21 2
0.039	66,750	5 0	2 08	32 1
0.032	67,050	6 0	2 39	39 1
0.026	67,050	5 3	2 67	48 1
0.022	67,350	7 3	3 51	56 8
0.018	67,700	6.0	2 77	69 5
0.013	67,500	6.5	3 13	96 2
0.009	67,750	3 3	1 16	139.
0.007	67,550	5 3	2 12	179.
0.006	66,700	2.0	0 69	217.

<sup>a</sup> Average of two tests.TABLE 5.—*Progressive Cold Rolling of Common Brass*

Thickness, Inch	Reduction Ratio $\frac{T_0}{T}$	Reduction, Per Cent $\frac{T_0 - T}{T_0} \times 100$	Brinell Hardness, 500-kg., 10-mm Ball
0.600	0 00	0 0	51
0.430	1 39	28 3	127 0
0.350	1 71	41 7	154.0
0.300	2 00	50 0	158 0
0.262	2 29	56 3	167 9
0.229	2 62	61 8	170 7
0.201	2 99	66 5	174 7
0.178	3 37	70.3	182 3
0.154	3 90	74 3	182.3
0.133	4.51	77.8	183.1
0.121	4.96	79.8	184.8
0.092	6 52	84.7	183.1
0.070	8.57	88.3	
0.060	10.0	90 0	183.3
0.052	11.5	91.3	184.6
0.046	13.0	92.3	186.9
0.040	15.0	93.3	189.1
0.036	16.7	94.0	193.1
0.033	18.2	94.5	193.0

reduction ratio of  $\frac{T_0}{T} = 150$ . Johnson<sup>9</sup> carried the rolling of copper to a ratio  $\frac{T_0}{T} = 45$ . Our maximum reduction ratio on copper was 217, and on brass 18.2. The authors, however, found their samples softening after a reduction  $\frac{T_0}{T} = 2.98$ . This would indicate that their metals were, in reality, hot worked at the thinner gages and that, in effect, the samples were partly annealed. This suggestion is strengthened by their statement that softening does not occur until all evidence of the original crystalline structure has been destroyed. In our work, we have found the original copper crystals quite distinct to a point beyond the reduction  $\frac{T_0}{T} = 20$ .

The authors state that their tests on rolled strips that differed in initial thickness show that specimens having the same ratio of reduction  $\frac{T_0}{T}$ , are not necessarily of the same hardness; this does not agree with the conclusions reached by others.<sup>10</sup> Commercial practice is based on the fact that the hardness of rolled copper and brass is relatively proportionate to the percentage reduction by rolling, regardless of thickness.

It is evident from rolling-mill experience with copper and brass that there is no reversal or softening point at a ratio of about 3 as indicated by the authors. Common practice has also made it evident that such a point must be above 5 if it exists. In the data submitted, however, no reversal or softening point has been found with copper below a ratio of 200 or with brass below a ratio of 18. Above these points the metal becomes so thin that the ordinary hardness tests are of no value.

JOHN LIVERMORE CHRISTIE, Fairfield, Conn.—Many rollers believe that if metal is rolled beyond a certain point its properties are spoiled and cannot be restored by annealing. I have never been able to find any scientific basis for that belief but this paper indicates that there might be some basis for it. However, on rolling some copper we obtained the same results as Mr. Bassett. We rolled two pieces of lake copper from 1 in. and  $\frac{5}{8}$  in., respectively. Those pieces were taken from the same bar and hot rolled down to these two sizes. They were then cold rolled down to 0.050 in., receiving reductions of 95 and 92 per cent., respectively. We had a little difficulty in getting accurate and reproducible Brinell hardness readings on the thinner metal, but we got quite definite indications of maxima at about 90 per cent. reduction by rolling, and about 80 per cent. on the two sizes. It is interesting to note that these maxima both came when the metal was about 0.080 in. thick.

<sup>9</sup> F. Johnson: *Jnl. Inst. Met.* (1920) 23, 443.

<sup>10</sup> C. H. Davis: *Proc. Am. Soc. Test. Mat.* (1917) 17, II, 166.

Tensile tests on the rolled samples did not show any drop; the tensile strength kept on going up. Some of the material that had been rolled (85, 90, 92, and 95 per cent.) was annealed at 700° C. for ½ hr. There was some indication that if metal is rolled beyond, say, 80 per cent. and

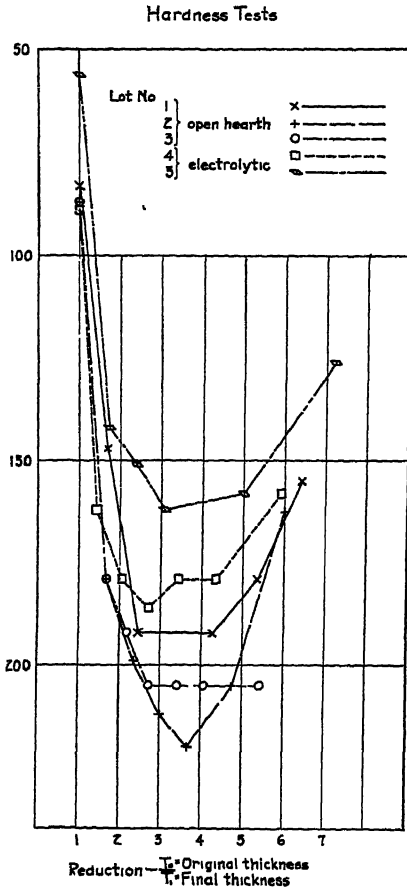


FIG. 11.—HARDNESS TESTS.

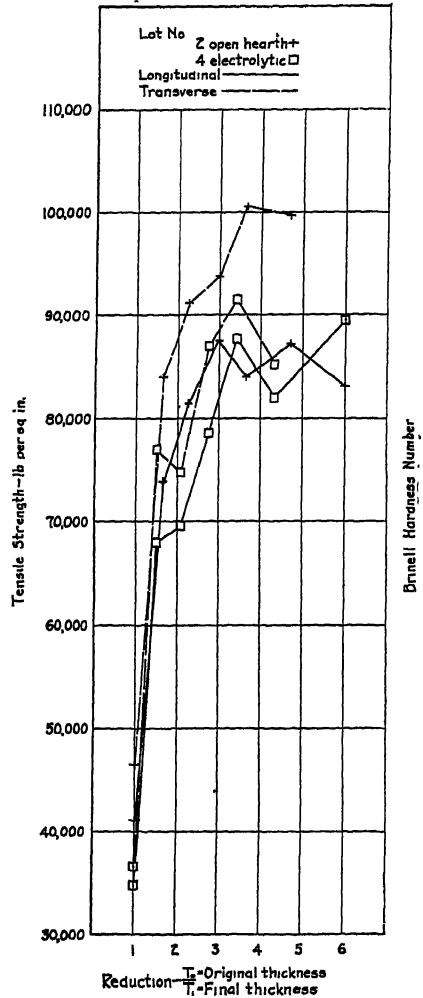


FIG. 12.—TENSILE TESTS.

then annealed the strength will not be quite as great as if the metal had not been rolled quite as hard; these figures, however, should be checked very carefully.

It is regrettable that the authors did not use the more conventional method of plotting the abscissas; that is, that they did not use the per

cent. reduction by rolling rather than the relation of original to final thickness.

The authors have suggested that their copper at the start was not thoroughly soft. There must be some other explanation for the results obtained when the stock was annealed at 100° because 100° would not soften copper whether it had been previously annealed or not.

JOHN R. FREEMAN, JR.,\* Washington, D. C.—The results of this investigation are of great interest to those concerned with rolling iron and steel as well as those interested in rolling non-ferrous metals. We have been carrying out, at the Bureau of Standards, a series of tests to determine the relative rolling characteristics of open-hearth deep-drawing stock and electrolytic iron and have obtained data that confirm the results presented by the authors. For the work, which I wish to discuss briefly, open-hearth steel strip obtained from three independent sources and two samples of electrolytic iron were used. These five lots of material were rolled under identical conditions in a commercial mill by a practical roller (of course, under our observation) and tests of the rolled material were carried out in the Bureau of Standards laboratories.

The original thickness of all stock was 65 mils (0.065 in.) and it was 3 in. wide. Coupons for tests were cut from the strip after each pass through the rolls. The following tests on the material have been made: Brinell hardness and tensile strength. The hardness tests were made with the same instrument used by the authors so that the results of the hardness tests are strictly comparable. The tensile tests were made on specimens the thickness of the material as rolled with 1 in. gage length and reduced section of  $1\frac{1}{2}$  in. width.

The results of the hardness tests are given in Fig. 11. The curves are plotted in the same manner as was used by the authors, to permit easy comparison. The general trend of the curves is the same as obtained by the authors. There is a preliminary hardening followed by a softening after a reduction of approximately 4 to 1. We were not aware of the authors' results at the time of rolling or we would have carried our total reductions further.

The results of the tensile tests are given in Fig. 12; it is to be regretted that the total reductions were not greater but I believe the curves indicate a similar effect. There is a preliminary increase in tensile strength with reduction; and if an average curve is drawn, it is apparent that at a reduction of approximately 3 to 1 the tensile strength tends to become constant, and possibly to decrease in value.

W. R. WEBSTER.—Was the material rolled dry or were the strips oiled during the passage through the rolls?

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\* Physicist, Bureau of Standards.

JOHN R. FREEMAN, JR.—The strips were well lubricated.

WILLIAM B. PRICE, Waterbury, Conn.—It seems to me that the reason for the apparent difference in the results obtained at the Bureau of Standards and in commercial work is largely due to the way in which the material is rolled; in commercial work, the rolls are water-cooled.

The explanation of the initial hardening obtained by the authors and by Mr. Freeman may be due to a temperature approximating somewhere between 100° and, possibly, 160° C. We all know that if, in the case of brass (Heyn first brought out that point) to relieve certain stresses that are responsible for season cracking, a relief heat treatment at comparatively low temperatures is given, it will increase the hardness.

In a paper by the speaker at the symposium on season cracking at the A. S. T. M., in 1919, that method was used to relieve strains, and the physical test shows an increase of from 2000 to 3000 lb. in the tensile strength. This whole problem is tied up with the question of self-annealing of the metal under certain conditions, which accounts for the softening obtained by the author.

Most of you are undoubtedly familiar with the Hooker cold-extrusion process used by the United States Cartridge Co., by which it gets a comparatively soft tube under certain conditions. I have been told that by changing the tools slightly it is possible to produce a hard or a soft tube at will.

NORMAN B. PILLING,\* E. Pittsburgh, Pa.—Mr. Christie said that at 100° C. you get no softening in copper; I think you may, if you have the proper amount of cold rolling. The rate-of-annealing curve rises very fast as you reach the amounts of rolling with which the authors have been concerned; and it is not improbable that at the reductions they used 100° C. is quite an active temperature for copper.

I know of an annealing test made after a reduction of about 70 per cent. with cooled rolls carried out in a commercial way. The metal was hard to begin with and lined up with the curve that Mr. Bassett has shown; it was annealed for 75 days at 100°, maintained by a thermostat, which resulted in a marked softening, a matter of 3 or 4 per cent.

D. J. McADAM, JR.,† Annapolis, Md.—As part of another investigation, at the Naval Engineering Experiment Station, we have recently made some hardness determinations on a number of ferrous and non-ferrous metals after various degrees of cold reduction in thickness. In these experiments, a great variety of carbon and alloy steels were used in the annealed and in the quenched and drawn conditions. The experi-

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\* Research Metallurgist, Westinghouse Electric & Mfg. Co.

† U. S. Naval Engineering Experiment Station.

ments also included a number of copper alloys, nickel, monel metal, and duralumin.

The material was reduced in thickness by compressing it in a 300,000-lb. Olsen tension and compression testing machine. The rate of reduction was much slower than the rate of reduction in thickness by rolling and the reduction could not be carried as far as in the authors' experiments.

Curves have been drawn in which abscissas represent percentage reduction in thickness and ordinates represent Brinell hardness; even in the most plastic material, the reduction by this method could not be carried beyond about 90 per cent.

The curves representing a number of kinds of material show a maximum Brinell hardness at about 70 to 80 per cent. reduction; this corresponds approximately with the authors' results. Such maxima were found in the following annealed materials: 0.25 per cent. carbon steel, 0.9 per cent. carbon steel, chrome-nickel steel, monel metal; also in hot-rolled nickel and monel metal and in quenched and drawn 0.35 per cent. carbon steel and chrome-molybdenum steel. No maxima, up to a 90 per cent. reduction, were found in annealed nickel, ingot iron, and annealed chrome-molybdenum steel.

It is possible that, if the reduction could have been carried further, maxima would have been found in some of the material that did not show maxima up to a reduction of 90 per cent. Some of these materials were apparently approaching a maximum hardness when a reduction of 90 per cent. was reached. In several instances, the annealed material did not show a maximum up to 90 per cent., whereas the hot-rolled or quenched material did.

An attempt was made, with ingot iron, to reach a greater percentage reduction by a modification of the original process of reduction. A cube of the metal was compressed about 10 per cent. in one direction and was then restored approximately to its original dimensions by compressing it in two directions perpendicular to the original direction. This process of compression and restoration was continued until the total percentage compression in the original direction was 80. At this point the cube was so distorted that this could not be continued. The distorted cube was then reduced in several stages without attempt at restoration until it had received a further reduction of about 70 per cent. Hardness determinations were made throughout the cold-working process. When these were plotted, as before, against total percentage reduction in the original direction, it was found that the graph was nearly a straight line, which did not appear to be approaching a maximum even after an amount of cold working that was plotted as 150 per cent. reduction on the same scale as the other graphs described. Further experiments will be made using the above described process of compression and restoration when



suitable dies have been made to prevent irregular distortion of the cubes of metal.

W. R. WEBSTER, Bridgeport, Conn.—Was there any rise in temperatures? If so, how much?

D. J. McADAM.—We did not observe that. We had to stop and cut the metal several times during the process of reduction; so the temperature could not have been very high.

F. G. SMITH, Waterbury, Conn.—I know of an instance when brass was drawn in the form of wire that it was so brittle that it could not be bent to a sharp angle, but after the wire was immersed in boiling water for a short time it could be bent as required. It was, thereby, made more ductile but it was not annealed in the sense that the metal became recrystallized.

ZAY JEFFRIES, Cleveland, Ohio.—In connection with overworking, a number of things must always be taken into consideration; and in the particular tests of the authors the method of testing is a most important thing to consider. From the standpoint of the internal structure of metals, two conditions are possible and, in fact, are pretty well known.

In the severe drawing of wire, a maximum in tensile strength is sometimes reached. The testing of wires is much more indicative of internal structure than the testing of sheets. Imagine the testing of a piece of foil; one can get any value desired depending on how the test is made. If one takes a piece of foil as wide as this room one can start to tear it at one side and get a low tensile strength. If the foil is cut down to a very thin strip, the normal tensile strength of the material can be approximated. So that in testing for tensile strength, the matter of tests on round wire is much more indicative of the internal structure than the tests on thin foil. Even in wire, there is a stage in the drawing when the tensile strength begins to decrease, the strength rises rapidly with the first working and then more slowly; and if worked far enough there is a decrease in tensile strength.

Two things may happen when the tensile strength decreases: Either the material becomes more brittle, as shown by a lower elongation; or it becomes more ductile, as shown by a higher elongation. In case a lower tensile strength is accompanied by a higher elongation, many people are ready to agree and admit that there is spontaneous annealing. On the other hand, if the lower tensile strength is associated with a lower elongation, we must look for the cause in internal rupture.

Internal rupture may be of two kinds: (1) shearing fissures, which may be seen in certain metals; and (2) the internal rupture at the slip planes, due to a weakened condition on the planes, such as we know

occurs in the case of iron and nickel and, in the cases cited by Bassett and Davis, on the increase in Brinell hardness and, Price and Davidson and Mathewson and Phillips on the increase in tensile strength of cold-worked alpha brass, by heating to a moderate temperature. The material is in a somewhat weakened condition but we cannot detect the weakness with a microscope.

Those things must always be taken into consideration in interpreting results such as the authors have obtained. We must also consider what may be the changes due to the preferential orientation of the crystal fragments produced by the very severe rolling. We are quite certain that one of the effects of preferential orientation is a lowering of the transverse sheet strength of a severely worked meta. What other effects it may have I am not prepared to say at the moment.

F. E. CARTER, Newark, N. J.—I do not entirely agree with some of the other speakers that self-annealing during rolling is the cause of this softening. I have made tests with copper and did not notice any of this apparent decrease in hardness. Also some years ago I made tests with chemically pure platinum, chemically pure gold, and silver; one would expect that, if this softening were due to self-annealing in the rolls, it might occur with silver and gold, which anneal at very low temperatures, and not with platinum. In no case was I able to find any indication of increasing softness on continued rolling.

HENRY S. RAWDON (authors' reply to discussion).—In publishing this note, the authors hoped that the results they had obtained would explain satisfactorily some of the contradictory statements in the technical literature as to the effect of severe cold-working on hardness, particularly as measured by the scratch method. The evidence presented and the opinions expressed in the discussion, however, indicate that the matter is far from being settled as yet.

As stated in the paper, the authors feel that the experimental data will not warrant very much theorizing as to the underlying fundamental cause and are not prepared, at present, to present a wholly satisfactory explanation of the phenomenon observed and the real meaning of the results. Hence it is impossible to explain the variance in the results obtained by Mr. Bassett and others from those of the authors. A considerable amount of work has been done by the authors since the completion of the manuscript, confirming the results presented here. Special attention was given to the matter of the temperature of the rolls and the specimen while being rolled. Briefly, it may be stated that while temperature does affect the *rate* at which hardening occurs upon rolling, the general form of the hardness-deformation curves obtained by the authors when the rolls and specimens were cooled with iced brine was the same as that typical of rolling carried out at room temperature.

The authors are in complete agreement with Doctor Jeffries that the method of testing is an important thing to consider. It is believed, however, that the scratch hardness method employed is affected less than any other, perhaps, by the form and thickness of the specimen tested and appears to be the most suitable to use in measuring the properties of very thin sheets. Without question, the tension test might well be expected to give very non-uniform and unreliable results. The same objection may perhaps be urged against those methods of hardness testing depending on indentation in which a rather heavy load is used. It can be demonstrated by suitable etching methods that the volume of metal distorted in any indentation hardness test is many times greater than the visible distortion as judged by the size of the indentation.

In answer to the criticism of the method of measuring the amount of reduction of the specimen by the working, it may be pointed out that there is no fundamental mathematical difference between the method used by the authors  $\left(\frac{T_0}{T}\right)$  and the conventional mill method  $\left(\frac{T_0 - T}{T_0} \times 100\right)$ . The second method, however, leads to very large numbers in the case of rolling very thin sheets, which is an inconvenience in the graphical representation on any small diagrams, such as those in this publication, of a change which is largely confined to a rather narrow range. The method used was chosen for this reason.

The interpretation of the observations, as recorded in the published photomicrographs, that not until the removal of evidence of the original crystalline by cold rolling was there softening of the metal, in support of the explanation by Mr. Bassett that the softening observed is to be attributed to partial annealing of the thin strips, is not clear. The authors believe that softening to the degree shown by some of the hardness curves directly after rolling, if it resulted from annealing, ought to be accompanied by a visible change in the structure.

As stated in the paper, the authors have other experiments relating to this subject either in progress or in contemplation. One has to do with the x-ray diffraction study and the determination of the effects of the preferential atomic orientation resulting from very severe deformation. This accords with the suggestion made by Doctor Jeffries in this discussion.

## Relation of Heat Treatment, Mechanical Properties, and Microstructure of 60-40 Brass

BY VICTOR O. HOMERBERG,\* P.D., CAMBRIDGE, MASS., AND  
DEXTER N. SHAW,† M.Sc., AKRON, OHIO

(New York Meeting, February, 1924)

A STUDY of the correlation of the mechanical properties and of the microstructure with the heat treatment of 60-40 brass has been confined, heretofore, to the rolled or extruded material as received from the manufacturer. The results obtained by Babson and Buhler,<sup>1</sup> Bengough and Hudson,<sup>2</sup> Stead and Stedman,<sup>3</sup> and Brayton<sup>4</sup> have been confined to the treatment of the material as received. No attempt was made to get the material into a given condition and then to work from this basis. To start with a given structure would have the decided advantage of making the work independent of the original condition, hence, to make the results reproduceable.

In a previous paper, it was shown, in connection with the study of the transformation that occurs at about 470° C., that if specimens were quenched to produce the beta structure and then reheated, the beta would begin to break down, at approximately 200° C., into a very finely divided alpha. It was predicted that important results might be obtained if test pieces were to be given a similar double heat treatment and then tested for the mechanical properties as well as a study of the microstructure. The material used in the present investigation was a 3/4-in. round bar of extruded muntz metal of the following composition: Copper, 61.05 per cent.; zinc (by difference), 38.90 per cent.; lead, 0.05 per cent.; iron, trace; tin, *nil*.

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† Research Laboratory, Goodyear Tire & Rubber Co.

<sup>1</sup> Babson and Buhler: "Effects that Different Temperatures of Annealing have on the Physical Properties of Brass and the Effects of Different Gases at the Annealing Temperatures on the Microstructure of Brass." M. I. T. Thesis, 1903.

<sup>2</sup> G. D. Bengough and O. F. Hudson: Heat Treatment of Copper-zinc Alloys. *Jnl. Soc. of Chem. Ind.* (1908) 27, 43 and 654.

<sup>3</sup> Stead and Stedman: *Op. cit.*

<sup>4</sup> H. M. Brayton: Heat Treatment of Beta Brasses. *Chem. & Met. Eng.* (1920) 22, 211.

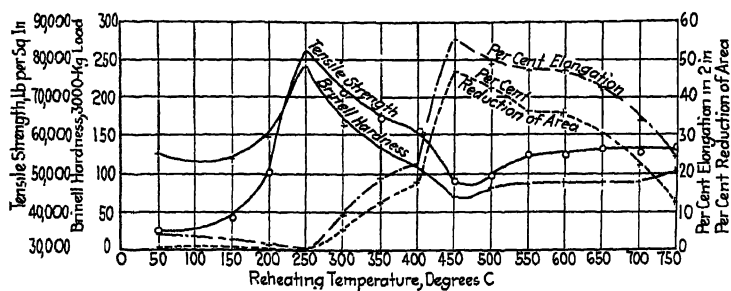


FIG. 1.—PHYSICAL PROPERTIES OF TEST SPECIMENS.

FIG. 2.—SPECIMEN NOT REHEATED.  $\times 250$ .FIG. 3.—SPECIMEN REHEATED AT 150° C.  
FOR 2 HR.  $\times 250$ .

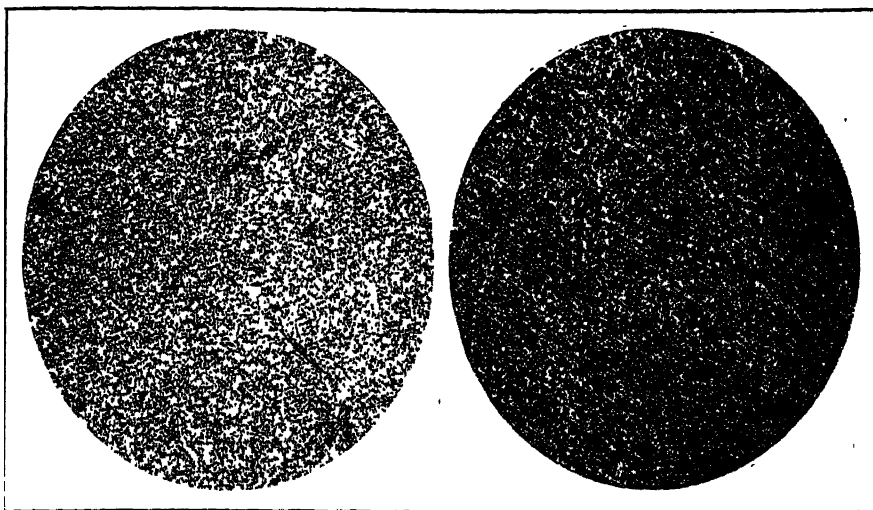


FIG. 4.—SPECIMEN REHEATED AT 200° C.  
FOR 2 HR.  $\times 250$ .

FIG. 5.—SPECIMEN REHEATED AT 250° C.  
FOR 2 HR.  $\times 250$

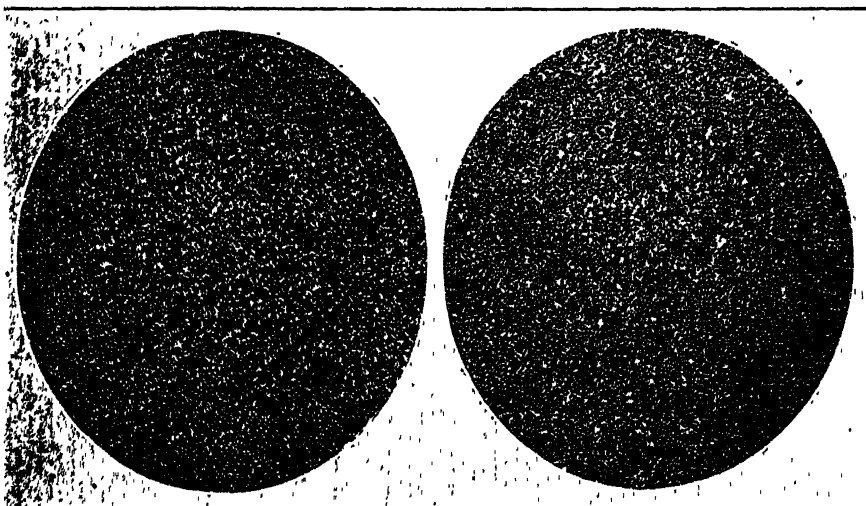


FIG. 6.—SPECIMEN REHEATED AT 300° C.  
FOR 2 HR.  $\times 250$ .

FIG. 7.—SPECIMEN REHEATED AT 350° C.  
FOR 2 HR.  $\times 250$ .

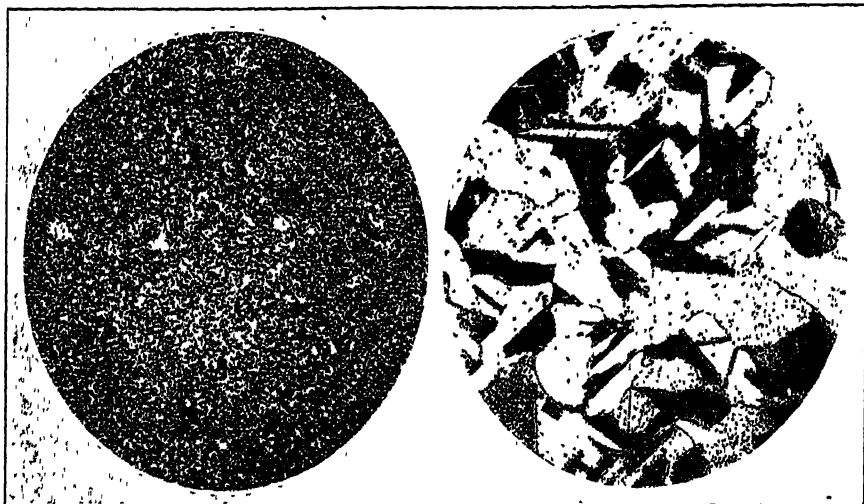


FIG. 8.—SPECIMEN REHEATED AT 400° C.  
FOR 2 HR.  $\times 250$ .

FIG. 9.—SPECIMEN REHEATED AT 450° C.  
FOR 2 HR.  $\times 250$ .



FIG. 10.—SPECIMEN REHEATED AT 500° C.  
FOR 2 HR.  $\times 250$ .

FIG. 11.—SPECIMEN REHEATED AT 550° C.  
FOR 2 HR.  $\times 250$ .



FIG. 12.—SPECIMEN REHEATED AT 600° C.  
FOR 2 HR.  $\times 250$ .

FIG. 13.—SPECIMEN REHEATED AT 650° C.  
FOR 2 HR.  $\times 250$ .



FIG. 14.—SPECIMEN REHEATED AT 700° C.  
FOR 2 HR.  $\times 250$ .

FIG. 15.—SPECIMEN REHEATED AT 750° C.  
FOR 2 HR.  $\times 250$ .



The test specimens were heated at 825° C. for 2 hr. and then quenched in iced brine, the temperature of which was -8° C. The tensile test pieces were machined to the standard specification of 0.505 in. diameter. These test bars were subsequently reheated for 2 hr. at temperature intervals of 50° C. from 150° to 750° C. and quenched in cold water.

The physical properties are given in Table 1 and the curves in Fig. 1; the structures are shown in Figs. 2-15, inclusive. All specimens were etched with concentrated  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  and photographed at 250 diameters. The results may be discussed by dividing the reheating temperatures into three groups; (a) 50°-250° C.; (b) 250°-450° C.; (c) 450°-750° C.

TABLE 1.—*Physical Properties of Test Specimens*

Reheating Temperature, Degrees C	Brinell Hardness		Tensile Strength, Lb per Sq In	Per Cent Elongation in 2 In	Per Cent Reduction of Area
	500-Kg Load	3000-Kg Load			
Original	119		62,000	35 0	36.7
50	97	126 0	35,000	4.0	0 6
150	100	123 0	38,750	3.0	0.4
200	136	149 0	52,500	1 0	0.2
250		241 0	82,750	0 0	0 0
300		163.0	71,250	9.0	5.4
350	130	131.0	65,000	19 0	12.5
400	119	111 0	61,250	22 0	17 5
450	69	68 0	48,750	55.5	46.7
500	74	82.5	50,000	49.0	42 2
550	74	85 5	55,000	47 0	36.4
600	76	87 1	55,000	47 0	36 0
650	79	88 7	56,750	42.5	30 4
700	85	88 7	55,750	34 0	22 0
750	96	107 0	57,000	24 5	12 6

The physical properties of these reheated specimens, as given in Table 1 and Fig. 1, show a rapid change when heated in the lower range. The tensile strength and the Brinell hardness increase rapidly from the first reheating temperature to 250° C., at which point they reach a maximum. The microstructure changes from crystals of beta, which exist until a temperature of 200° C. is reached, to finely divided alpha; an increase in tensile strength and hardness is to be noted with this change. The structure is finely divided alpha at 250° C., at which temperature the material exhibits remarkable mechanical properties; *i. e.*, maximum hardness and tensile strength with no ductility. Properties analogous to those of martensite in steel are clearly evident. A tensile strength of 82,750 lb. per sq. in. and a Brinell hardness of 241 under a 3000-kg. load are greater than any values previously recorded; these

values were checked and are reproduceable. The microstructure showed characteristic grain boundary alpha along the edges of the fracture, thereby indicating an intercrystalline break. All the specimens that were quenched for beta contained a slight fringe of alpha at the grain boundaries.

In the temperature range from 250° to 450° C., the tensile strength and the hardness decrease to a minimum while the ductility passes through a maximum. It will be noted from Figs. 5-8 that the finely divided alpha has coarsened with an increase in the reheating temperature. At 450° C. there is a sudden increase in the ductility, as a result of the recrystallization of the alpha into twin crystals. Fig. 9 shows that

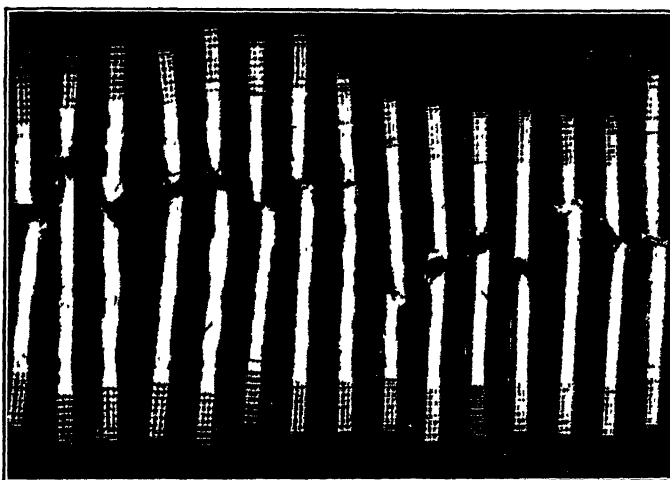


FIG. 16.—TEST BARS AND THEIR FRACTURES.

practically the entire microstructure consists of twinned alpha. The result is a high value for elongation at the expense of hardness. The tensile strength is 48,750 lb. per sq. in.; the hardness is 68 under a 3000-kg. load; the elongation and the reduction of area are 55 and 46.7 per cent., respectively.

The third range from 450° to 750° C. shows a gradual increase in tensile strength and in Brinell hardness. Figs. 10-15 show that the proportion of beta has gradually increased. Alpha needles are obtained on quenching from 750° C. Fig. 15 shows beta with unabsorbed alpha twins and needlelike alpha, which is characteristic of the alpha that comes out of the beta on quenching. Fig. 16 shows the fractured test bars.

The effect of the time of heating at the quenching temperature on the Brinell hardness after reheating at 250° C. for 2 hr. was studied. Table 2 indicates the heat treatment and the results obtained:

TABLE 2.—*Heat Treatment and Results Obtained*

Quenching Temperature, Degrees C	Time at Quenching Temperature, Hours	Brinell Hardness after Reheating at 250° C. (3000 Kg.)
750	$\frac{1}{4}$	149
	$\frac{1}{2}$	156
	1	159
	2	166
775	$\frac{1}{4}$	170
	$\frac{1}{2}$	179
	1	179
	2	179
800	$\frac{1}{4}$	170
	$\frac{1}{2}$	179
	1	179
	2	179
825	$\frac{1}{4}$	170
	$\frac{1}{2}$	179
	1	179
	2	179

At 750° C., the alpha reeds, which were present in the original extruded material, persisted throughout the grains even after 2 hr. heating. The needlelike alpha was distributed throughout the beta during the short times of heating but was present only at the grain boundaries when the time of heating was 2 hr. At 775°, 800°, and 825° C., the original alpha reeds were absorbed even after heating for 15 minutes.

The effect of various quenching media was studied. The test pieces were heated at 825° C. for 2 hr., then quenched in different media. They were then reheated at 250° C. for 2 hr., quenched in water, and the physical properties determined. Table 3 gives the results obtained; they show

TABLE 3

Quenching Medium	Tensile Strength, Lb per Sq. In.	Per Cent. Elongation in 2 In.	Brinell Hardness, 3000 Kg.
Brine at -8°C. . . . .	82,750	0.0	241.0
Water at 25°C. . . . .	62,000	12.0	179.0
Water at 100°C. . . . .	57,500	44.0	74.0
Cold oil. . . . .	58,200	34.5	85.7

that the only medium that is satisfactory for maximum hardness and tensile strength is iced brine. The beta grains existed in the specimens quenched in water at 25° C. but these were surrounded by large alpha

fringes and alpha needles within the grains. The specimens quenched in boiling water and in oil showed no beta as distinct grains.

The effect of the time of reheating at 250° C. was studied by quenching test bars in iced brine after heating for 2 hr. at 825° C. and then reheating for different lengths of time at 250° C. Table 4 gives the results obtained; they show that the breaking down of the beta is very rapid.

TABLE 4  
TIME AT 250° C.                      HARDNESS (3000 Kg.)

15 min . . . . .	229
30 min . . . . .	229
1 hr . . . . .	241
2 hr . . . . .	241

The effect of the various rates of cooling from the reheating temperature of 250° C. was studied by quenching test bars in iced brine after heating for 2 hr. at 825° C. and then quenching in different media after reheating at 250° C. for 2 hr. The results given, in Table 5, show that the hardness and the tensile strength are practically independent of the rate of cooling from the reheating temperature.

TABLE 5

Quenching Medium	Brinell Hardness, 3000 Kg.	Tensile Strength, Lb per Sq. In	Per Cent. Elongation in 2 In.
Cold water. . . . .	241	82,750	0
Air... . . . .	229	81,750	0
Cold oil. . . . .	229		
Iced water . . . . .	241		

### SUMMARY

If brass in the beta condition is used, a gradual increase in hardness and in tensile strength and a gradual decrease in ductility are obtained on reheating the quenched material to 250° C. Between this temperature and 450° C., the reverse is true. From 450° to 750° C., there is a slight increase in hardness and in tensile strength and a decrease in ductility.

The maximum tensile strength of 82,750 lb. per sq. in. and the maximum hardness of 241 with no elongation were obtained at 250° C.; the structure showed very fine alpha and the fracture was intercrystalline.

The maximum elongation of 55.5 per cent. in 2 in. with the lowest Brinell hardness of 68 under a 3000-kg. load and the lowest tensile strength of 48,750 lb. per sq. in. were obtained after reheating to 450° C.; the structure showed only alpha twins and the break was transcrystalline. The Brinell hardness and the tensile strength are proportional.

Satisfactory beta was obtained when the specimen was heated for any length of time greater than  $\frac{1}{2}$  hr. at any temperature greater than 775° C. This fact is important, as all of the specimens for which values are given in Table 1 showed a very large grain size. It may, therefore, be possible to get even better values for material treated under such conditions as to obtain a very small grain size. The treatment mentioned above is suggestive.

The specimens must be quenched in iced brine in order to procure maximum hardness and tensile strength on reheating. The change from beta into alpha at 250° C. is rapid. The rate of cooling from 250° C. has no appreciable effect on the physical properties.

## Relation of Heat Treatment to the Microstructure of 60-40 Brass

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CAMBRIDGE, MASS.

(New York Meeting, February, 1924)

ON SEVERAL occasions, when 60-40 brass is first obtained in the beta condition by quenching at about 825° C. and is then reheated, the writers have noticed that recrystallization will take place in the form of twin crystals at the grain boundaries of the original beta crystals. It was, therefore, thought that interesting results would be obtained if this twinning process was studied further, especially as to the temperature at which it first occurs. The material used in the investigation was a bar of extruded muntz metal,  $\frac{1}{2}$  in. in diameter, and of the following composition: Copper, 60.21 per cent.; zinc, 39.73 per cent.; lead, trace; iron, trace; tin, *nil*.

Specimens 1 in. in length were sawed from this bar and a hole was drilled into the side of each specimen until it reached the center, and the tip of a platinum-platinum rhodium thermocouple was inserted. A small Hoskins' resistance-type electric furnace was used for heating the specimens.

The specimens were first heated at 840° C. for 2 hr. and then quenched in cold water, in order to get the material entirely in the beta state. In every case, in the reheating process, the furnace was brought to the desired temperature before the specimen was introduced. The time occupied in preheating was from 20 to 30 min. By sawing back  $\frac{1}{4}$  in. on each side of the hole, two parts were obtained from each specimen and duplicate observations were possible. The specimens were held at the reheating temperatures for periods of 15 min., 30 min., 1, 2, and 4 hr. All specimens were etched with a freshly prepared mixture of equal volumes of concentrated  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$ .

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A reheating of the quenched specimen resulted in a breakdown of the beta into finely divided alpha. Figs. 1 and 2 show this condition in the specimens reheated at 440° C. for  $\frac{1}{2}$  hr. and 1 hr. respectively. No indication of the production of alpha twins was apparent in these specimens.

Carpenter<sup>1</sup> has shown that there is a thermal change at about 470° C., as first determined by Roberts-Austen<sup>2</sup> but attributed to experimental defects in the apparatus by Shepherd,<sup>3</sup> Tafel,<sup>4</sup> and Bornemann.<sup>5</sup> Carpenter detected this critical point pyrometrically by both heating and cooling

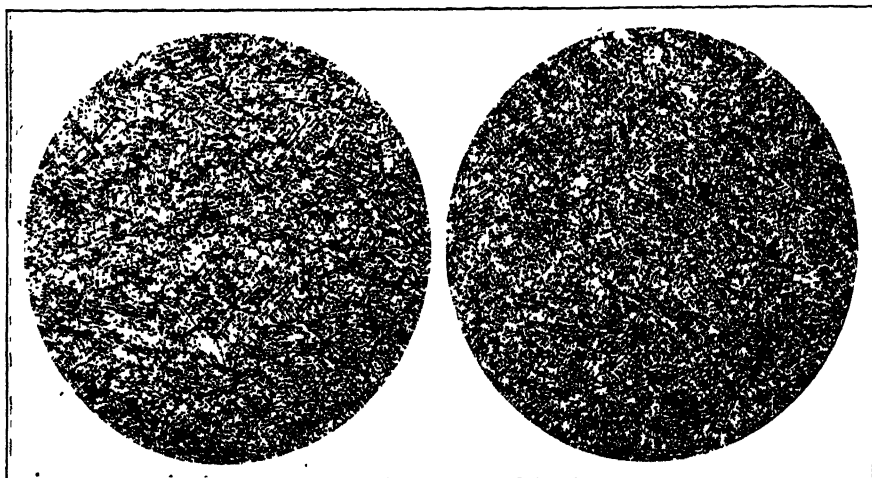


FIG. 1.—SPECIMEN REHEATED AT 440° C. FOR 30 MIN.  $\times 100$ . FIG. 2.—SPECIMEN REHEATED AT 440° C. FOR 1 HR.  $\times 100$ .

curves in all alloys of copper and zinc ranging from 63 to 40 per cent. copper. He concluded that at 470° C., on cooling, beta splits up into alpha and gamma.

Stead and Stedman<sup>6</sup> subjected specimens of cast and cold-rolled muntz metal to prolonged heating of three months at 430° C. and for 984

<sup>1</sup> H. C. H. Carpenter and C. A. Edwards: A New Critical Point in Copper Zinc Alloys. *Jnl. Inst. of Metals* (1911) 5, 127-149.

<sup>2</sup> Roberts-Austen: Fourth Report to the Alloys Research Committee of the Institution of Mechanical Engineers (1897) 31-100.

<sup>3</sup> E. S. Shepherd: The Constitution of the Copper-zinc Alloys. *Jnl. Phys. Chem.* (1904) 8, 421.

<sup>4</sup> V. E. Tafel: *Metallurgie* (1908) 5, 378.

<sup>5</sup> K. Bornemann: *Metallurgie* (1909) 6, 247.

<sup>6</sup> J. E. Stead and H. G. A. Stedman: Muntz Metal. *Jnl. Inst. of Metals* (1914) 11, 119-134.

hr. at 270° C., but failed to detect any clear evidence of segregated gamma and, therefore, held the tentative view that the disappearance of the beta constituent was due entirely to solution in the alpha.

The critical point was again considered by Hudson,<sup>7</sup> who contended that the heat effect must be due to a polymorphic transformation of the beta constituent from beta to beta prime, and advanced evidence to support his belief. Hudson gave evidence of the formation of

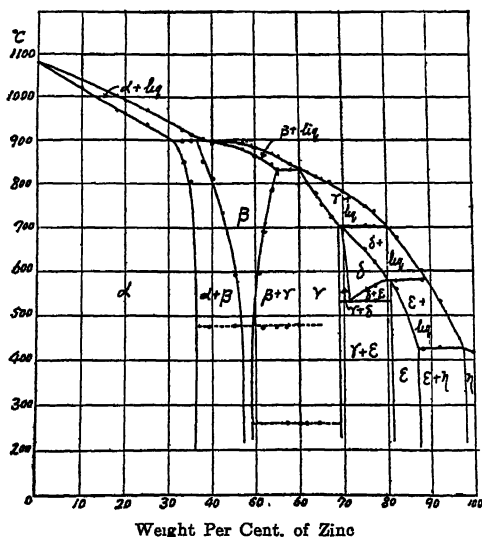


FIG. 3.—EQUILIBRIUM DIAGRAM OF COPPER-ZINC SYSTEM.

beta prime by annealing alpha + gamma at temperatures below the critical point.

Recently an equilibrium diagram of the copper-zinc system has been obtained by Imai,<sup>8</sup> chiefly by means of electric-resistance measurements. This diagram, Fig. 3, nearly coincides with those of Shepherd and Tafel. As to the transformation of the beta constituent, Imai obtained a negative result for a eutectoid separation or an allotropic change.

A significant result of the present investigation is that recrystallization is shown to begin at about 460° C. The first indication of recrystallization, in the form of twinning at the grain boundaries of the original beta crystals, is shown in Fig. 4; this specimen was reheated at 465° C. for 2 hr. In Fig. 5 is shown a specimen reheated at 455° C. for 80 hr.;

<sup>7</sup> O. F. Hudson: The Critical Point at 460° C. in Zinc-copper Alloys. *Jnl. Inst. of Metals* (1914) 12, 89-101.

<sup>8</sup> Imai: Equilibrium of the Copper-zinc System. *Sci. Repts. Tohoku Imperial Univ.*, 11, 313-332.



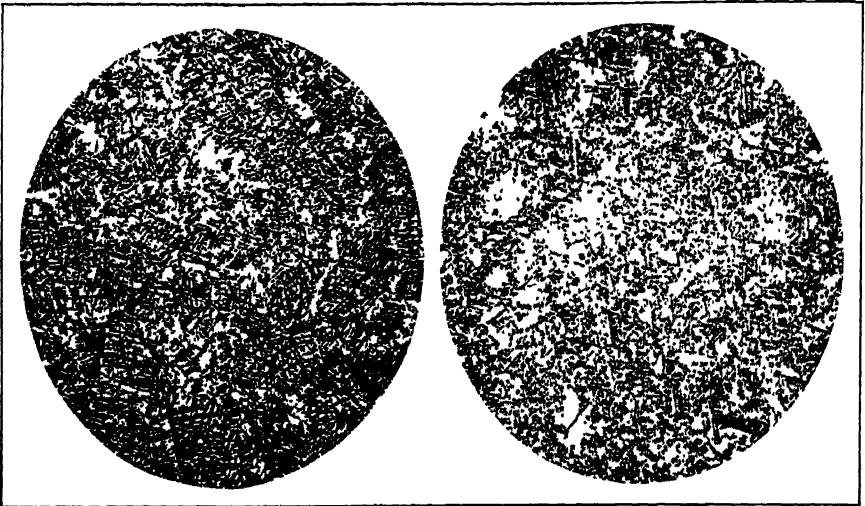


FIG. 4.—SPECIMEN REHEATED AT 465° C.  
FOR 2 HR.  $\times 100$ .

FIG. 5.—SPECIMEN REHEATED AT 465° C.  
FOR 80 HR.  $\times 100$ .

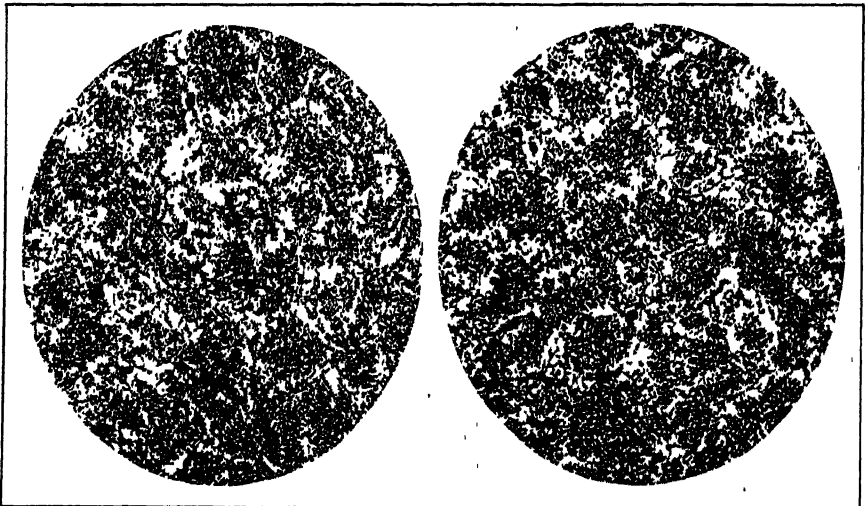


FIG. 6.—SPECIMEN REHEATED AT 495 °C.  
FOR 15 MIN.  $\times 100$ .

FIG. 7.—SPECIMEN REHEATED AT 495° C.  
FOR 30 MIN.  $\times 100$ .

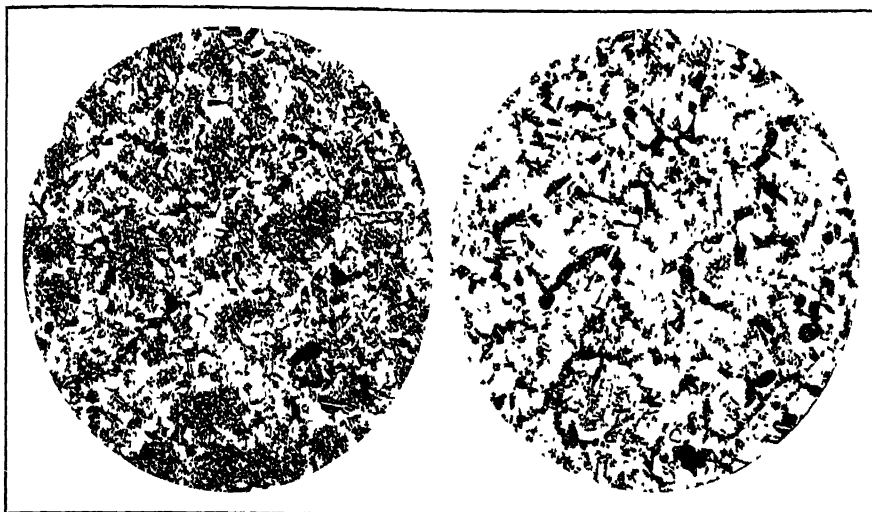


FIG. 8.—SPECIMEN REHEATED AT 495° C.  
FOR 1 HR.  $\times 100$

FIG. 9.—SPECIMEN REHEATED AT 500° C  
FOR 2 HR.  $\times 100$ .

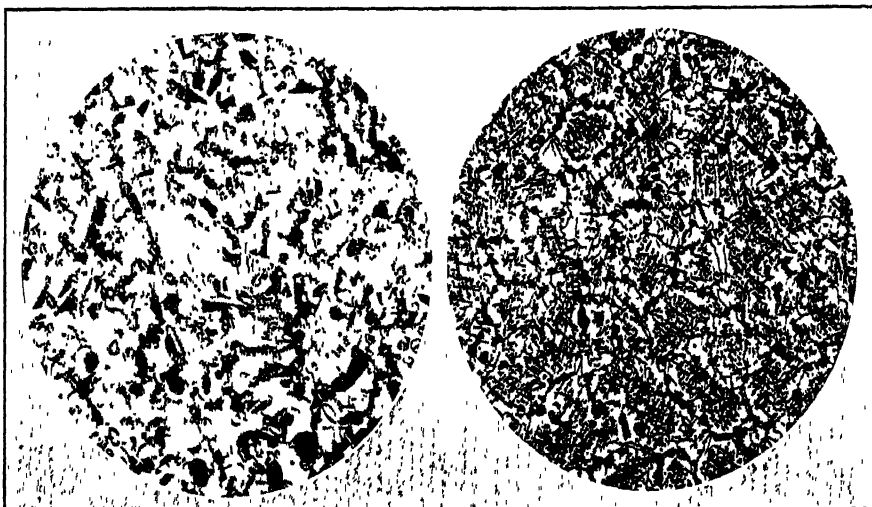


FIG. 10.—SPECIMEN REHEATED AT 500° C.  
FOR 4 HR.  $\times 100$ .

FIG. 11.—SPECIMEN REHEATED AT 530° C.  
FOR 15 MIN.  $\times 100$ .



FIG. 12.—SPECIMEN REHEATED AT 530° C.  
FOR 30 MIN.  $\times 100$ .

FIG. 13.—SPECIMEN REHEATED AT 530° C.  
FOR 1 HR.  $\times 100$ .

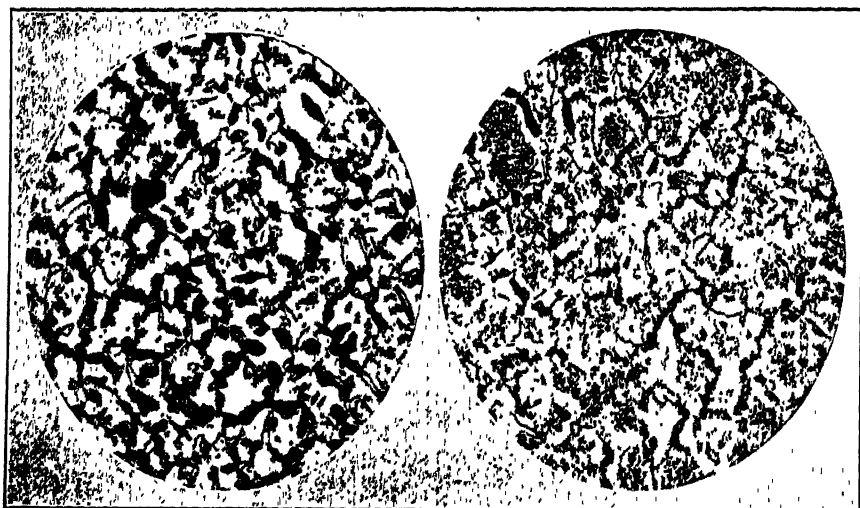


FIG. 14.—SPECIMEN REHEATED AT 530° C.  
FOR 2 HR.  $\times 100$ .

FIG. 15.—SPECIMEN REHEATED AT 575° C.  
FOR 15 MIN.  $\times 100$ .

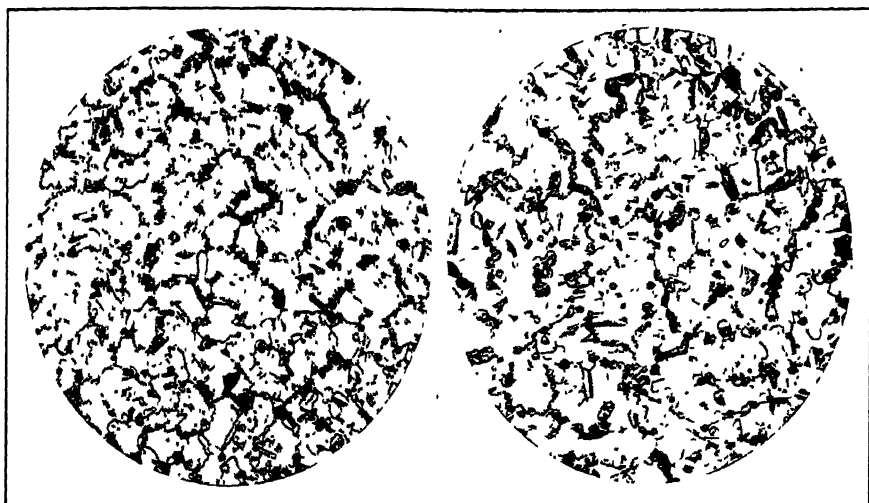


FIG. 16.—SPECIMEN REHEATED AT 575° C.  
FOR 30 MIN.  $\times 100$ .

FIG. 17.—SPECIMEN REHEATED AT 575° C.  
FOR 1 HR.  $\times 100$ .



FIG. 18.—SPECIMEN REHEATED AT 575° C.  
FOR 2 HR.  $\times 100$ .

FIG. 19.—SPECIMEN REHEATED AT 575° C.  
FOR 4 HR.  $\times 100$ .

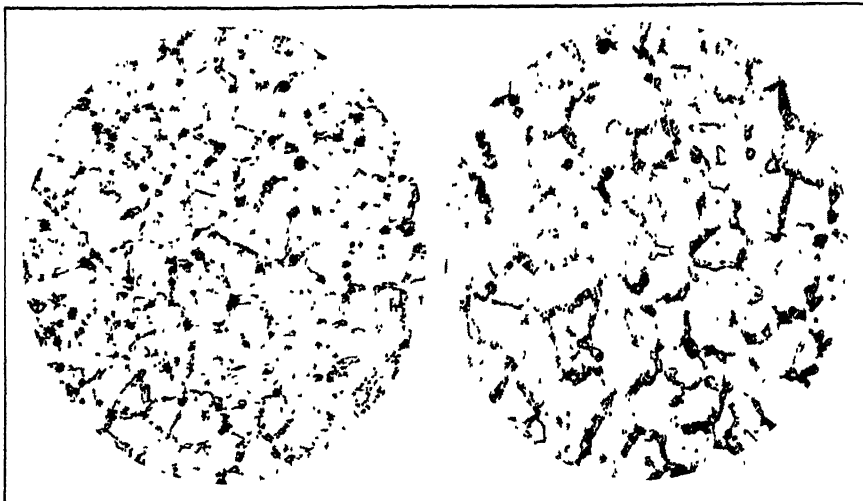


FIG. 20.—SPECIMEN REHEATED AT 605° C.  
FOR 15 MIN.  $\times 100$ .

FIG. 21.—SPECIMEN REHEATED AT 605° C.  
FOR 45 MIN.  $\times 100$ .

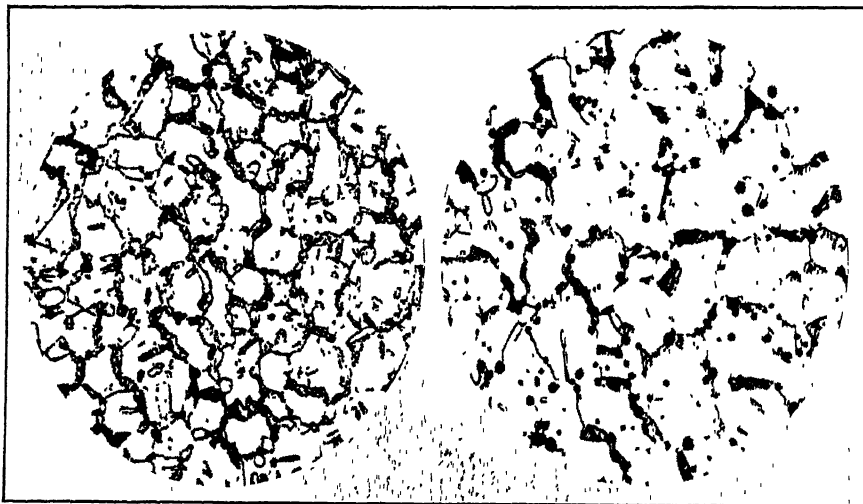


FIG. 22.—SPECIMEN REHEATED AT 605° C.  
FOR 1 HR.  $\times 100$ .

FIG. 23.—SPECIMEN REHEATED AT 605° C.  
FOR 2 HR.  $\times 100$ .

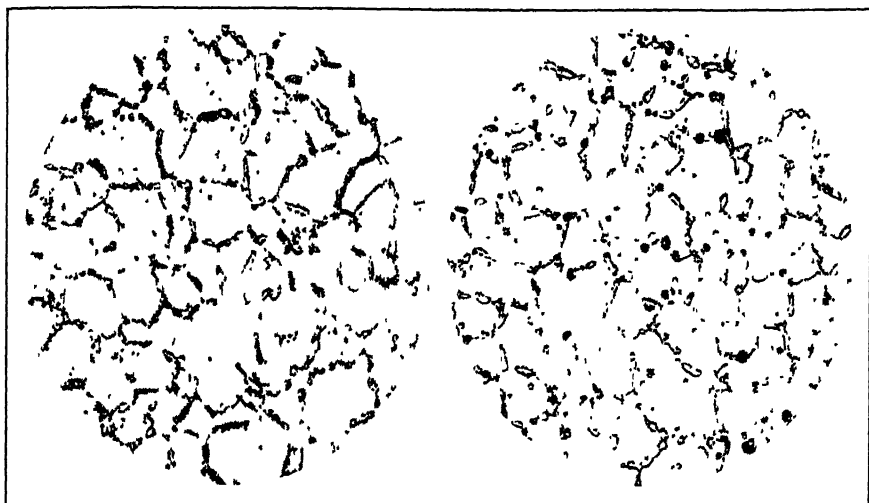


FIG. 24.—SPECIMEN REHEATED AT 660° C.  
FOR 15 MIN.  $\times 100$ .

FIG. 25.—SPECIMEN REHEATED AT 660° C.  
FOR 30 MIN.  $\times 100$ .

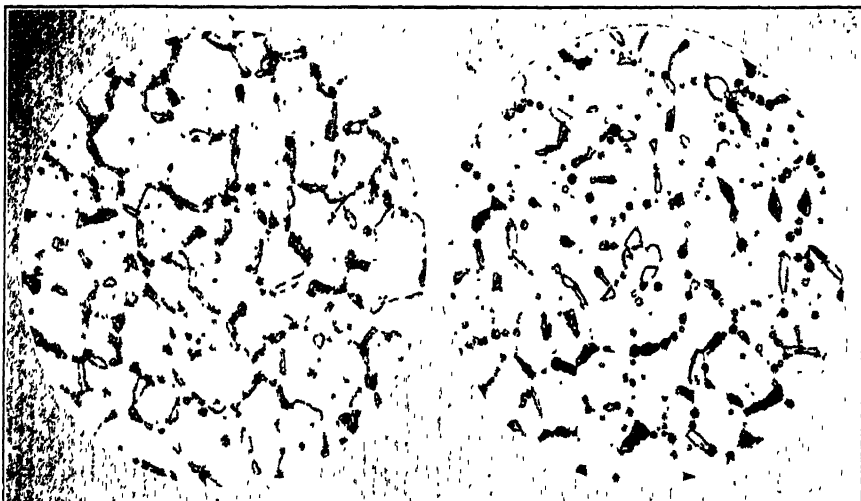


FIG. 26.—SPECIMEN REHEATED AT 660° C.  
FOR 1 HR.  $\times 100$ .

FIG. 27.—SPECIMEN REHEATED AT 660° C.  
FOR 2 HR.  $\times 100$ .



FIG. 28.—SPECIMEN REHEATED AT 660° C.  
FOR 4 HR.  $\times 100$ .

FIG. 29.—SPECIMEN REHEATED AT 150° C.  
FOR 2 HR.  $\times 250$

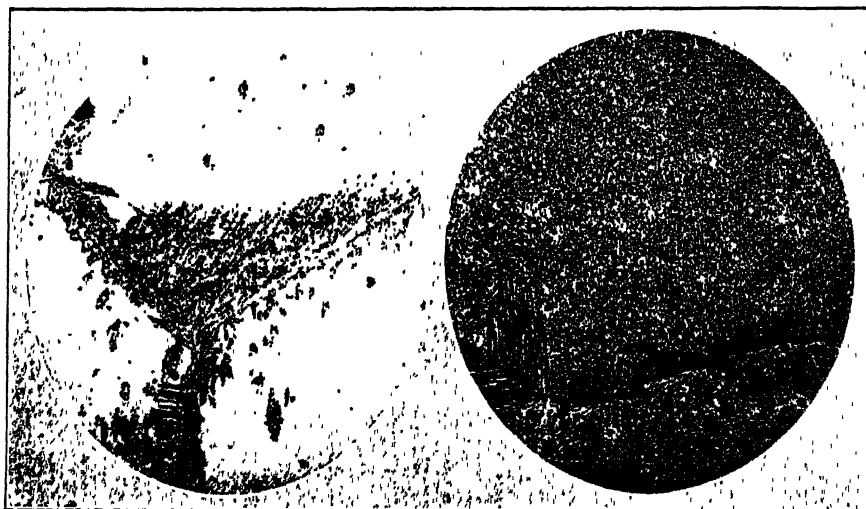


FIG. 30.—SPECIMEN REHEATED AT 200° C.  
AND QUENCHED IN WATER.  $\times 250$ .

FIG. 31.—SPECIMEN REHEATED AT 200° C.  
FOR 1 HR.  $\times 250$ .

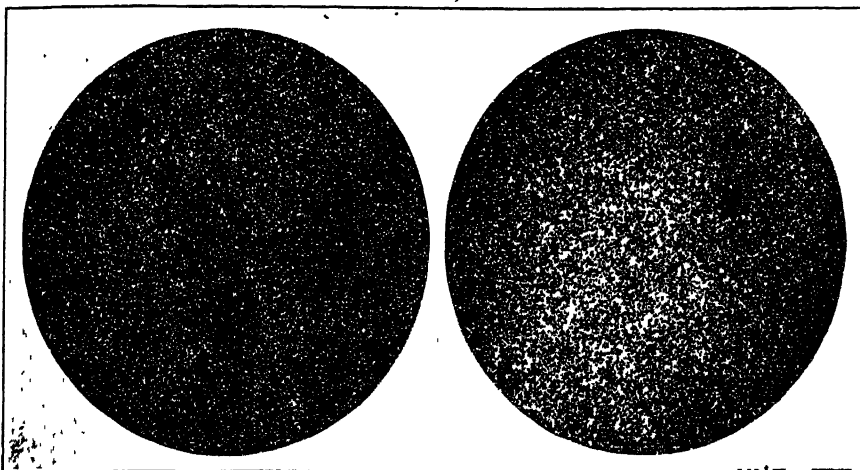


FIG. 32.—SPECIMEN REHEATED AT 200° C.  
FOR 2 HR.  $\times 250$ .

FIG. 33.—SPECIMEN REHEATED AT 300° C.  
FOR 3 HR.  $\times 250$ .

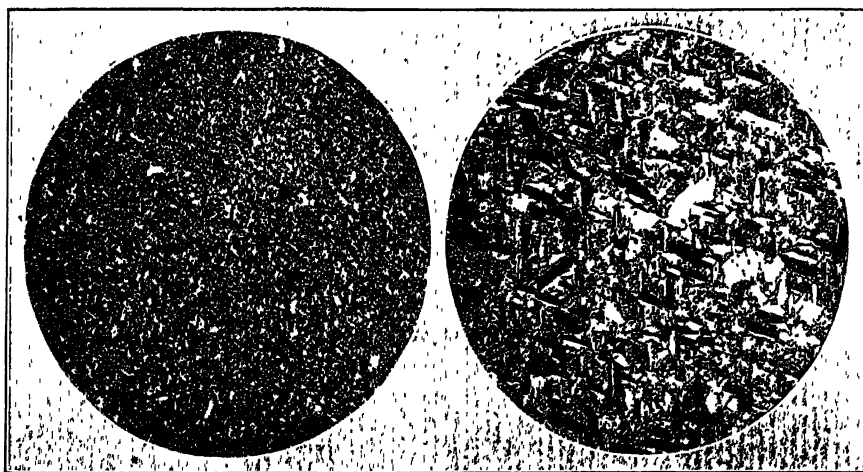


FIG. 34.—SPECIMEN REHEATED AT 400° C.  
FOR 2 HR.  $\times 250$ .

FIG. 35.—SPECIMEN REHEATED AT 460° C.  
FOR 2 HR.  $\times 250$ .





FIG. 36.—SPECIMEN REHEATED AT 500° C.  
FOR 2 HR.  $\times 250$ .

FIG. 37.—SPECIMEN REHEATED AT 600° C.  
FOR 2 HR.  $\times 250$ .

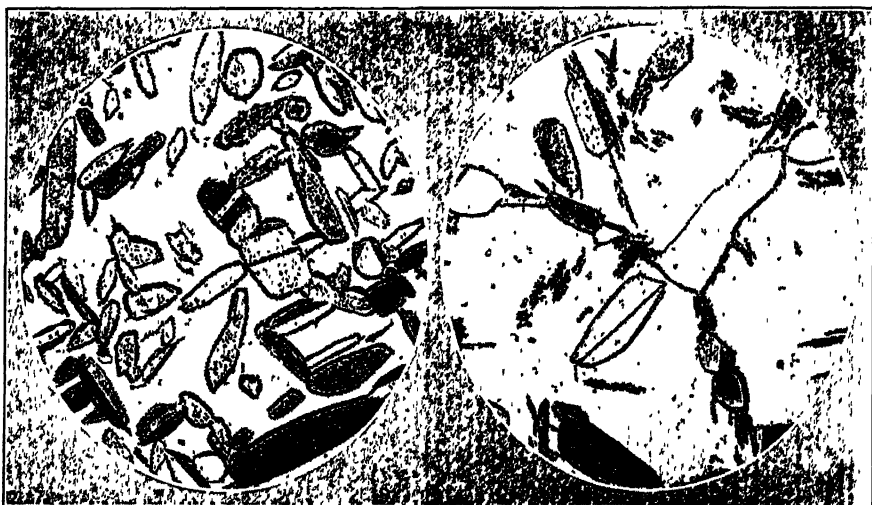


FIG. 38.—SPECIMEN REHEATED AT 700° C.  
FOR 2 HR.  $\times 250$ .

FIG. 39.—SPECIMEN REHEATED AT 750° C.  
FOR 2 HR.  $\times 250$ .

this shows a number of alpha twins together with considerable needlelike alpha. The present writers were unable to obtain the gamma constituent in 60-40 brass.

The presence of alpha twins at the grain boundaries of the original beta grains becomes more marked as the temperature and the time of reheating are increased; the various stages are shown in Figs. 6 to 28. The appearance of the fine boundaries of the beta grains and unabsorbed alpha is shown in Figs. 27 and 28. All specimens were quenched in water from the reheating temperature.

To corroborate the results obtained with bar No. 1, another rod was selected, sawed into specimens, and prepared in the same manner. The composition of the bar was: Copper, 61.05 per cent.; zinc (by difference), 38.90 per cent.; lead, 0.05 per cent.; iron, trace; tin, *nil*.

All of the specimens were heated at 825° C. for 2 hr. and quenched in cold brine and then reheated at the following temperatures: 150, 200, 300, 400, 460, 500, 600, 700, and 750° C. One set was quenched as soon as the reheating temperature was reached. Other specimens were held at the respective temperatures for periods of  $\frac{1}{2}$ , 1, 2, and 4 hr. and then quenched in water. Figs. 29 to 39 show the structures obtained.

Again, there resulted a breakdown of the beta into a very fine alpha, which closely resembles martensite as shown in Fig. 34. Finely divided alpha was obtained after reheating at 200° C. for 1 hr. The beta grains with fringes of alpha at the grain boundaries are shown in Figs. 29 and 30. In almost every case, with the exception of the specimens prepared from bar No. 1, an alpha fringe was obtained after quenching in an attempt to obtain beta alone. This alpha fringe seldom, if ever, forms twin crystals on annealing but gradually goes into solution as the reheating temperature is increased. This fact is rather remarkable inasmuch as the alpha resulting from the breakdown of the beta forms twin crystals of alpha at about 460° C. as shown in Fig. 35.

If extruded material is annealed, the alpha masses will ultimately form twin crystals. If this extruded material is heated into the beta range, cooled in the furnace, and then reheated, the resultant alpha masses will not form twin crystals but will gradually go into solution to form beta as the reheating temperature is increased. If the material containing the alpha fringes at the grain boundaries is compressed, the fringed alpha will form twin crystals on annealing, as would be expected from the well-known fact that mechanical work and annealing are both necessary for the production of twinned alpha. The fact that twinned alpha results from the annealing of quenched beta must imply that the operation of quenching is, in this case, equivalent to working. In this connection, attention is again called to the fact that the fringe of alpha does not form these twin crystals. The alpha must be worked before it will form twin crystals on annealing; this phenomenon is well

known. It seems strange, therefore, that the alpha resulting from the breakdown of the beta, on reheating, should form twin crystals and that the fringe of alpha does not form these twin crystals.

Another interesting fact was observed when working with bar No. 1. In the discussion of Carpenter's paper, it was stated that muntz metal should be heated at 850° C. for 5 hr. and then quenched under very definite conditions in order to obtain beta free from alpha. Specimens from bar No. 1 were heated at 830° C. for periods varying from 15 min. to 4 hr. and quenched in cold brine. The specimen that was quenched after 15 min. heating showed no alpha. All of the specimens were practically free from alpha at the grain boundaries; this result would indicate that

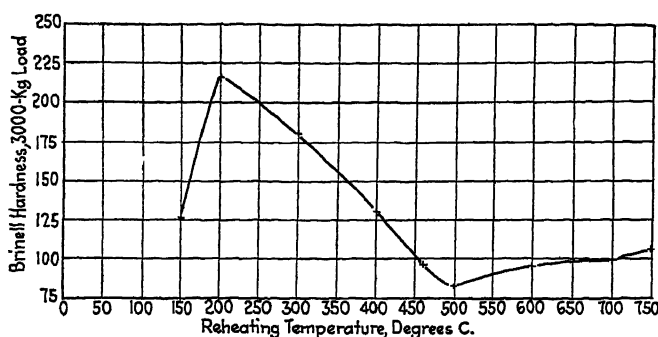


FIG. 40.—BRINELL HARDNESS AT VARIOUS REHEATING TEMPERATURES.

the rate of cooling is the important factor to consider and that 5 hr. heating, as suggested by Carpenter, is unnecessary.

Fig. 36 shows the structure to be almost entirely twinned alpha. As the temperature is increased the proportion of beta also increases. Fig. 39 shows the presence of both twinned alpha, which represents alpha that has not been absorbed, and granular alpha, which is the alpha that comes out of the beta on quenching.

REHEATING TEMPERATURE, DEGREES C.	BRINELL HARDNESS (3000 Kg.)	REHEATING TEMPERATURE, DEGREES C.	BRINELL HARDNESS (3000 Kg.)	REHEATING TEMPERATURE, DEGREES C.	BRINELL HARDNESS (3000 Kg.)
150	126	400	131.0	600	90.3
200	217	460	92.0	700	99.2
300	179	500	87.1	750	111.0

It is obvious that a range of mechanical properties might be anticipated from the various structures obtained on reheating. Brinell hardness values were determined on the specimens from rod No. 2. The accompanying table and Fig. 40 show interesting results for Brinell hardness under a 3000-kg. load. It will be noted that the maximum hardness is obtained at a reheating temperature of 200° C.; and as the structure becomes coarsened, the hardness values drop, reaching a minimum

between 460 and 500° C. This minimum value is at the point at which the structure is practically all twinned alpha; the hardness increases slowly as the proportion of beta increases. The time of reheating for the specimens that were tested was 2 hours.

### CONCLUSIONS

Specimens of 60-40 brass, when quenched to form beta, break down into finely divided alpha at approximately 200° C. This alpha gets coarser as the reheating temperature is increased and forms twinned alpha at 450-460° C. At this temperature the material consists almost entirely of alpha twins. The twin crystals form first at the grain boundaries of the original beta grains, provided there is no alpha fringe at these boundaries. As the reheating temperature is increased, beta becomes more prominent because of the absorption of the alpha.

The alpha fringe is gradually absorbed without the formation of twin crystals as the reheating temperature is increased. This fringe will form twin crystals if it is subjected to cold work before it is annealed.

The alpha masses in extruded 60-40 brass form twin crystals on annealing, but such is not the case with material heated at 825° C., cooled slowly in the furnace, and then annealed.

The Brinell hardness is a maximum at the point where the alpha resulting from the breakdown of the beta is in the most finely subdivided state. It is a minimum at the temperature at which the material consists of twinned alpha; it increases again as the quantity of beta increases.

A wide range of mechanical properties is predicted for 60-40 brass when subjected to a double heat treatment.

### DISCUSSION

O. W. ELLIS, Toronto, Ont. (written discussion).—Early in 1921, the writer had occasion to undertake a number of experiments on the reheating of quenched alpha-beta brass. Prior to carrying out these tests he made experiments with the view of determining the approximate lower limit of copper contained in the alpha solid solution at about 400° C., this being the temperature at which he was intending to carry out the reheating of the alpha-beta brasses. Three alloys were annealed at 400° C. for a period of 28 days, the alloys containing 57.40, 59.44 and 61.06 per cent. of copper, respectively. Analyses were made of the alloys subsequent to the prolonged annealing, so that care was taken to eliminate any question as to loss of zinc by volatilization during the prolonged heating. It was found that the 61.06-per cent. alloy was completely free from the beta constituent while the structures of the other alloys were as shown in Figs. 41 and 42, which were presented by the writer at the

opening meeting of the London section of the Institute of Metals in February, 1921. Since this date, the writer has assumed all brasses containing above 60 per cent. of copper to be in reality alpha brasses.

In the reheating experiments referred to above, the writer treated the quenched 61.06 per cent. brass at 400° C. and he is able fully to confirm the findings of the authors that fine-grained alpha is produced as a result of the reheating at 400° C. of quenched brass of this composition.

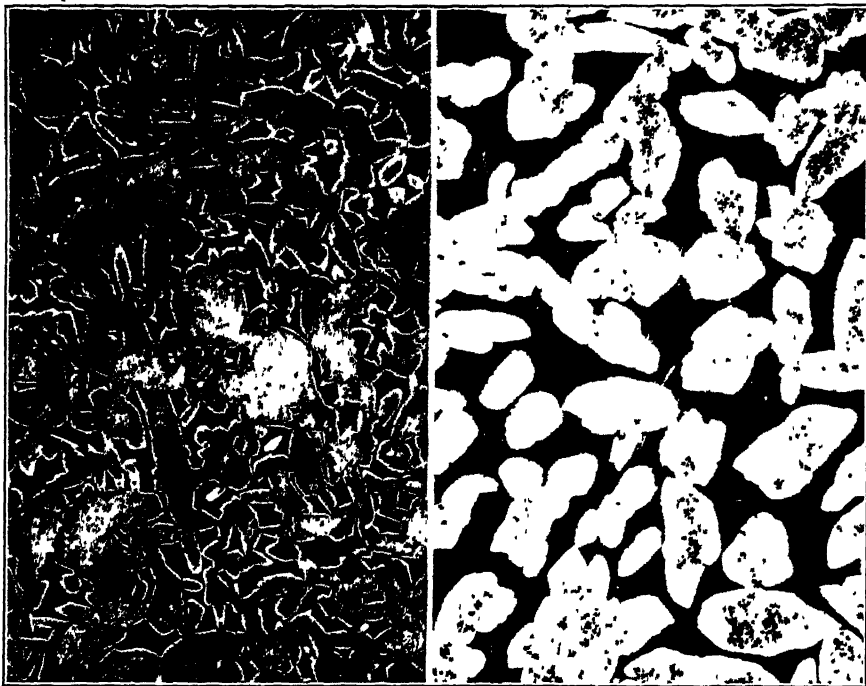


FIG. 41.—59.44-PER CENT. COPPER ALLOY, HEATED AT 400° C. FOR 28 DAYS; ETCHED WITH FERRIC CHLORIDE.  $\times 75$ .

FIG. 42.—57.40-PER CENT. COPPER ALLOY, HEATED AT 400° C. FOR 28 DAYS; ETCHED WITH FERRIC CHLORIDE.  $\times 75$ .

The reheating of true alpha-beta brasses at 400° C., those containing less than about 60 per cent. of copper, results, however, in the production of a totally different type of structure. Alpha is, in most cases, precipitated within and around the beta crystal grains. The resulting alloy is, on this account, extremely fragile and of low tenacity. Whether reheating at higher temperatures than 400° C. (the maximum used by the author in his experiments) would result in an improvement of the mechanical characteristics of the quenched alpha-beta alloys, the writer is unable to say. There is a wide field for investigation in this connection, and the authors are to be congratulated on the pioneer work they have done.

## Corrosion of Brass as Affected by Grain Size\*

BY ROBERT J. ANDERSON,† MET. E., PITTSBURGH, PA., AND GEORGE M. ENOS,‡  
MET. E., CINCINNATI, OHIO

(New York Meeting, February, 1924)

THIS paper gives a summary of tests made on the accelerated electrolytic corrosion of the tin brass, 70:29:1 copper-zinc-tin (admiralty metal), of different grain sizes in various electrolytes. There has been great difference of opinion as to the effect of grain size on the corrosion rate of brass, particularly in condenser-tube practice, but so far as is known no information has been published on the subject. It has been assumed, on the basis of the amorphous-cement theory, that fine-grained brass would corrode more rapidly than coarse-grained because the amorphous phase is more soluble than the crystalline and there is more cement per unit area exposed in the fine-grained material.

In previous work on the corrosion of metals and alloys in acid mine waters from coal mines,<sup>1,2</sup> it was found that the grain size, within a restricted range, had practically no effect on the corrosion of the brass 70:29:1 copper-zinc-tin. In the tests made, samples of three grain sizes were included; viz., 0.025, 0.035, and 0.075 mm. diameter (1600, 817, and 177 gr. per sq. mm., respectively), and the average losses on exposure to the most acid of three waters were 7.07, 6.80, and 6.72 mg. per sq. cm. per day (24 hr.), respectively. No distinguishing features were observed on microscopic examination of the corroded samples. In two other mine waters, the corrosion losses were substantially the same for the respective samples. These tests were incidental to other tests and were not sufficiently comprehensive to warrant drawing definite conclusions. In further work with the accelerated electrolytic corrosion test, as developed recently in the Bureau of Mines, tests were made

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\* Published by permission of the Director, Bureau of Mines of the Department of the Interior.

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<sup>1</sup> W. A. Selvig and G. M. Enos: Corrosion Tests on Metals and Alloys in Acid Mine Waters from Coal Mines. *Bull. 4*, Coal-Mining Investigations Series, Carnegie Inst. of Tech., Pittsburgh (1922).

<sup>2</sup> R. J. Anderson and G. M. Enos: Microstructural Aspects of Metals and Alloys Corroded by Acid Mine Water. *Bull. 5*, Coal-Mining Investigations Series, Carnegie Inst. of Tech., Pittsburgh (1923).

on 70:29:1 copper-zinc-tin alloy of different grain sizes, in the form of tubes and sheets, in six corroding media.

The writers wish to acknowledge the aid given by J. R. Adams in the laboratory work.

#### MATERIALS USED FOR TESTING

The materials used for testing were commercial tubes and sheets of varying grain size, furnished through the courtesy of brass manufacturers. The tubes were admiralty condenser tubing  $\frac{3}{4}$  in. in diameter, 0.065 in. wall thickness, and 18 in. long, and varied in grain size by intervals of about 0.01 mm. from 0.01 to 0.10 mm. The grain sizes were produced by definite anneals of hard-drawn tubing. The average composition of the material was: Copper 70.34 per cent., lead 0.01 per cent., iron 0.03 per cent., tin 1.34 per cent., zinc (by difference) 28.28 per cent.

The sheet samples were in the form of strips 3 in. wide by 6 in. long, No. 16 B. & S. gage, and of different grain size. The composition of these samples was: Copper 70.80 per cent., lead 0.055 per cent., iron 0.026 per cent., tin 1.05 per cent., zinc (by difference) 28.069 per cent. The grain sizes were: 0.015 mm., obtained by annealing for 30 min. at 400° C. a strip that had been rolled to size following an anneal at 400° C.; 0.250 mm., obtained by annealing at 800° C. a strip that had been rolled to size following an anneal at 800° C.; uneven grain structure of 0.015 to 0.068 mm. obtained by annealing at 400° C. a strip that had been rolled to size following an anneal at 800° C.; and 0.250 mm., with distorted grains obtained by rolling to size a strip that had been annealed at 800° C.

#### METHOD OF TESTING

The method of testing was the accelerated electrolytic corrosion test, developed by the writers and J. R. Adams<sup>3</sup> in the Bureau of Mines. In this test, the metal or alloy to be tested for corrosion is made the anode in the corroding medium (this must be an electrolyte) and platinum wire is used for the cathode. Any simple type of electrolytic apparatus with rotating spindle connections may be employed, and the speed of rotation should be capable of control. The imposed current is passed through the electrolytic cells in series in the case of a multiple-cell apparatus, and the current may be regulated by a lamp-bank resistor. The cells are heavy-walled glass beakers of about 500 c.c. capacity.

Samples for test may be prepared of any convenient size, say 10 to 60 sq. cm. of exposed surface. Heavy copper wires are soldered to the test samples for connection to the anode spindles. The test piece

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<sup>3</sup> R. J. Anderson, G. M. Enos, and J. R. Adams: Accelerated Corrosion Testing of Metals and Alloys, with Special Reference to Acid Mine Waters. *Bull.* 6, Coal-Mining Investigations Series, Carnegie Inst. of Tech., Pittsburgh (1923).

should be run for a sufficient period of time to yield a weighable loss; most commercial metals and alloys will show a decided loss in 8 hr. in most electrolytes. Record is kept of the weight of the test piece before and after corrosion, the area of the exposed portion, the current imposed, the voltage drop per cell, the chemical analysis of the test piece, the chemical analysis of the electrolyte, and the nature of the coatings and precipitates formed. For various reasons, the current density should be preferably about 0.18 amp. per sq. dm. of surface exposed. Speed of rotation, current, time, and other factors may be varied to suit conditions.

In the tests on the tubes and sheets, six electrolytes were used; viz., (1) acid mine water, containing 2020 p.p.m. of free sulfuric acid (plus sulfates of iron and aluminum not determined); (2) dilute sulfuric acid, 15,760 p.p.m.; (3) sea water, 4 per cent. sea salt by weight; (4) aqueous sodium-chloride solution, 8 per cent. NaCl by weight; (5) aqueous sodium-hydroxide solution, 1 per cent. NaOH by weight; and (6) tap water, containing 8 p.p.m. of calcium carbonate. There were thus two acid solutions, two alkaline solutions, and two neutral salt solutions. With few exceptions, the test pieces were run in duplicate and both the tube and sheet samples were corroded in the above electrolytes. The speed of rotation was 140 r.p.m. and the temperature was  $20^{\circ} \pm \text{C}$ .

For the tubes, test pieces were cut about  $2\frac{1}{4}$  in. long, and an area of 40 to 50 sq. cm. was exposed to the corroding media. A current sufficient to give a current density of not over 0.2 amp. per sq. dm. was used, and the nominal amperage may be taken as 0.11–0.12 amp. per sq. dm. of exposed surface area. The samples were exposed in the various electrolytes for 6 hr. Before immersion, the test pieces were measured and weighed, and the proper depth of immersion calculated. After being corroded, the samples were washed in running water and cleaned with a stiff bristle brush, dried, and again weighed. The area over which corrosion took place was then calculated from final measurements.

For the sheet brass, strips were cut  $\frac{1}{2}$  by 3 in. in size, and an area of about 14 sq. cm. was exposed to the corroding medium. The current density was 0.16–0.17 amp. per sq. dm. on the average. Analyses were made of the coatings formed and the electrolytes after corrosion for certain of the tests, but these were not run for all because the results showed only that the tendency is to corrode copper and zinc in amounts proportionate to the nominal composition.

## RESULTS OF TESTS

The data for the corrosion of the tube samples are plotted in Fig. 1. The average values for the duplicate runs are plotted, and the curves show the loss in weight per unit current density vs. the grain size. The ordinate figures were obtained by dividing the total loss in weight by the



current density for the various grain sizes, and this yields convenient figures for comparison. For direct comparison, the loss in mg. per sq. cm. per day is also convenient, but this does not take account of slight variations in current density.

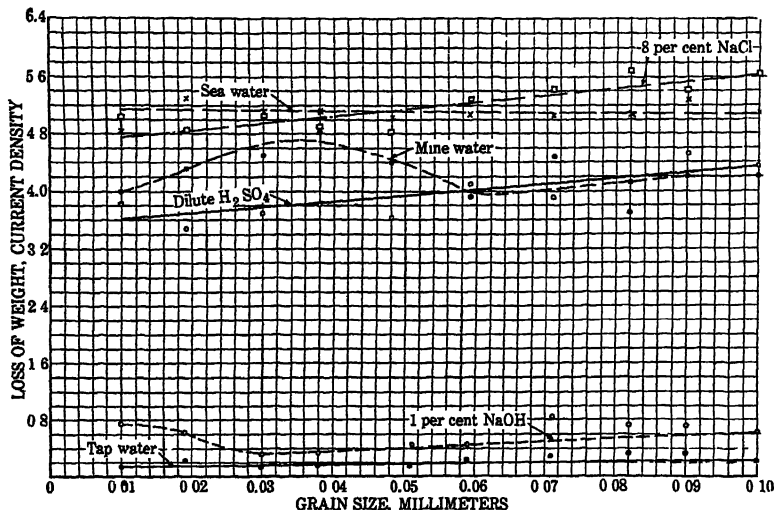


FIG. 1.—EFFECT OF GRAIN SIZE ON CORROSION LOSS OF ADMIRALTY TUBING IN SEVERAL ELECTROLYTES (ACCELERATED ELECTROLYTIC TEST).

### DISCUSSION OF RESULTS

Examination of the curves shows that for the tubes there is slight increase of corrosion with increasing grain size in 8 per cent. sodium chloride and dilute sulfuric acid. The grain size had practically no effect on the corrosion loss in sea water and tap water. In mine water, the curve is irregular; this is to be expected because of the complex nature of the water and the hydrolysis that occurs. In sodium hydroxide, there is a marked drop in loss at grain size of 0.03 mm. in diameter.

For the sheet, the fine-grained samples (0.015 mm.) had the least loss in sodium hydroxide and in dilute sulfuric acid, while in mine water the large-grained (worked) samples had the smaller loss. In the salt-water solutions, the fine-grained samples had a slightly smaller loss.

It should be emphasized that the actual loss in weight on corrosion in any of the media is but slightly affected by the grain size. Comparison of the relative losses of the tubes and sheet cannot be made because the current densities employed were different and also because of variation in methods of working and annealing. It is possible to compare the relative order of loss by grain size in the same solution but not the actual loss.

Lack of space prevents extended discussion of the nature of the precipitates formed in the cells and on the anodes and cathodes in the tests. In practically all cases, some copper was deposited on the cathodes. The acid solutions turned blue quickly and maintained that color during the

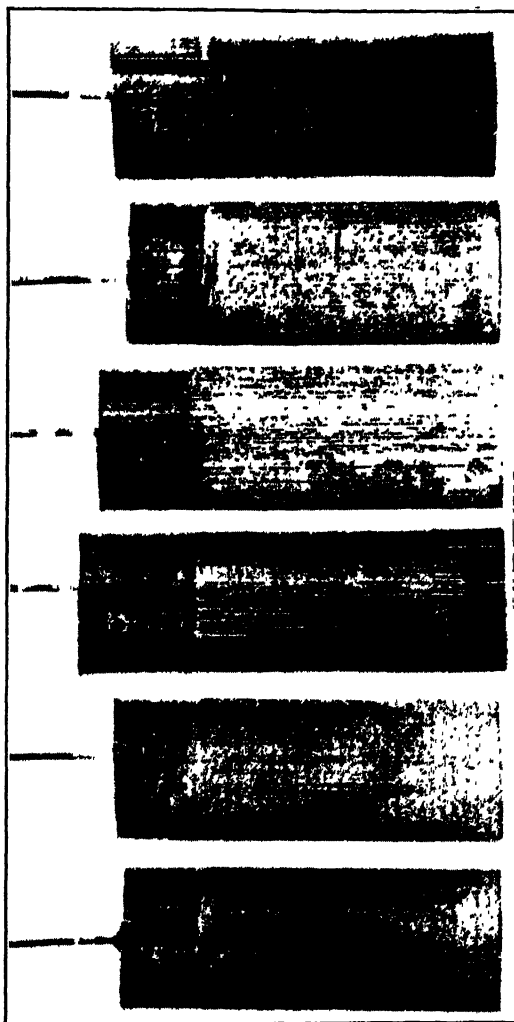


FIG. 2.—GROUP OF TYPICAL TUBE SAMPLES, CORRODED IN DIFFERENT ELECTROLYTES, ALL HAVING GRAIN SIZE OF 0.082 MM. DIAMETER; (a) CORRODED IN  $H_2SO_4$ ; (b) MINE WATER; (c)  $NaOH$  SOLUTION; (d) SEA WATER; (e)  $NaCl$  SOLUTION; AND (f) TAP WATER; ALL CLEANED; ALL ACTUAL SIZE

test runs, and the anodes became copper red in color. In the salt solutions, large quantities of flocculent precipitates formed, probably basic chlorides; these were variable in color with orange predominating. Scale was formed on the anodes in the salt solutions. The loose coatings on the anodes formed in the acid and salt solutions were easily removed

in cleaning. In the basic electrolytes, thin coatings formed on the anodes; these seemed to inhibit corrosion.

### MICROSCOPY OF CORRODED SAMPLES

After cleaning, the corroded samples were examined ocularly and also at 75 diameters under a binocular microscope, and selected samples were studied microscopically at high magnification. Fig. 2 shows a group of six typical tube samples, all of the same grain size, 0.082 mm., corroded

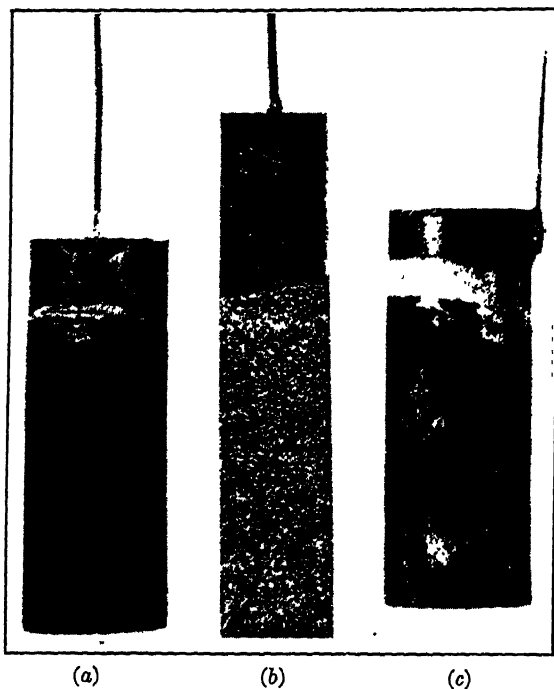


FIG. 3.—GROUP OF CORRODED SAMPLES; (a) TUBE CORRODED IN SEA WATER, NOT CLEANED; (b) SHEET, NaCl SOLUTION, CLEANED; (c) TUBE, SEA WATER, NOT CLEANED; ALL ACTUAL SIZE.

in the different electrolytes; these samples were cleaned before being photographed. In Fig. 3 (a) is a tube after corrosion in sea water; this was not cleaned. The deposit on the surface was copper red in color and apparently was copper or copper oxide or a mixture of both. Fig. 3 (b) is a sheet sample corroded in 8-per cent. sodium-chloride solution, after cleaning; and (c) is a tube, not cleaned, after corrosion in sea water, showing a band of scale formed at the water line. The band was pale blue in color, but below it the coating was typical copper red.

It is convenient, in discussing the microscopy of the corroded samples, to consider the effects given in the acid, basic, and neutral solutions.

Visual and microscopic examination revealed certain definite characteristics for the tube and sheet samples in the different electrolytes.

### *Acid Solutions*

The microscopic features of the tube and sheet samples corroded in mine water and sulfuric acid were similar. Etching effects resulted from the corrosion, as is shown in Fig. 4 (a), (b), and (c), the grain structure being developed by the acid attack. The central portion of (c) is shown in (d), at higher magnification; the structure appears "pearlitic." A nodular structure with very fine pitting, somewhat similar to (d), is shown in (e); in (f) cracks developed on the inside edge of a tube are shown. In general, the corrosion of the alloy in sulfuric-acid solutions is characterized by very fine pits, uniformly distributed, and by an etching effect that develops the internal structure. Cracks may be formed on the edges of tubes, but these are not so pronounced or numerous as when corrosion takes place in sodium-chloride solutions.

### *Sodium-chloride Solutions*

Corrosion of tube and sheet samples in sea water and sodium-chloride solution gave similar effects, Fig. 5 (a) shows a nodule of brass left on the corroded surface of a tube, the darker areas are copper or copper oxide; (b) shows a similar sample of smaller grain size; (c) shows the etching pattern produced on a sheet sample corroded in sea water; and (d) a similar sheet corroded in the sodium-chloride solution; (e) shows brass nodules left *in situ*, the surface is finely pitted; (f) shows the intergranular cracks set up on the inside edge of a tube sample by the sodium-chloride solution. Aside from the coatings formed, corrosion of the material in sea water and the sodium-chloride solution is characterized by the "splotchy" or patchwork appearance of the surface, where the brass may be left as nodular masses, or the whole surface may be evenly attacked. Many small pits are formed. Etching effects are noted, particularly on the sheet. The coatings usually consist of copper, or copper oxide, below the water line; at the line, and above, a scale, or coating, may form; this consists probably of basic chlorides.

### *Alkaline Solutions*

Corrosion in tap water and sodium-hydroxide solution gave similar microstructural features on examination, Dark brown coatings having a glazed appearance were formed on the samples; these were uniform in appearance to the naked eye. Fig. 6 (a) shows the surface of a tube corroded in tap water; while the surface appeared smooth to the eye, deep ridges and pits were noted at 300 diameters. In (b), the surface of a tube

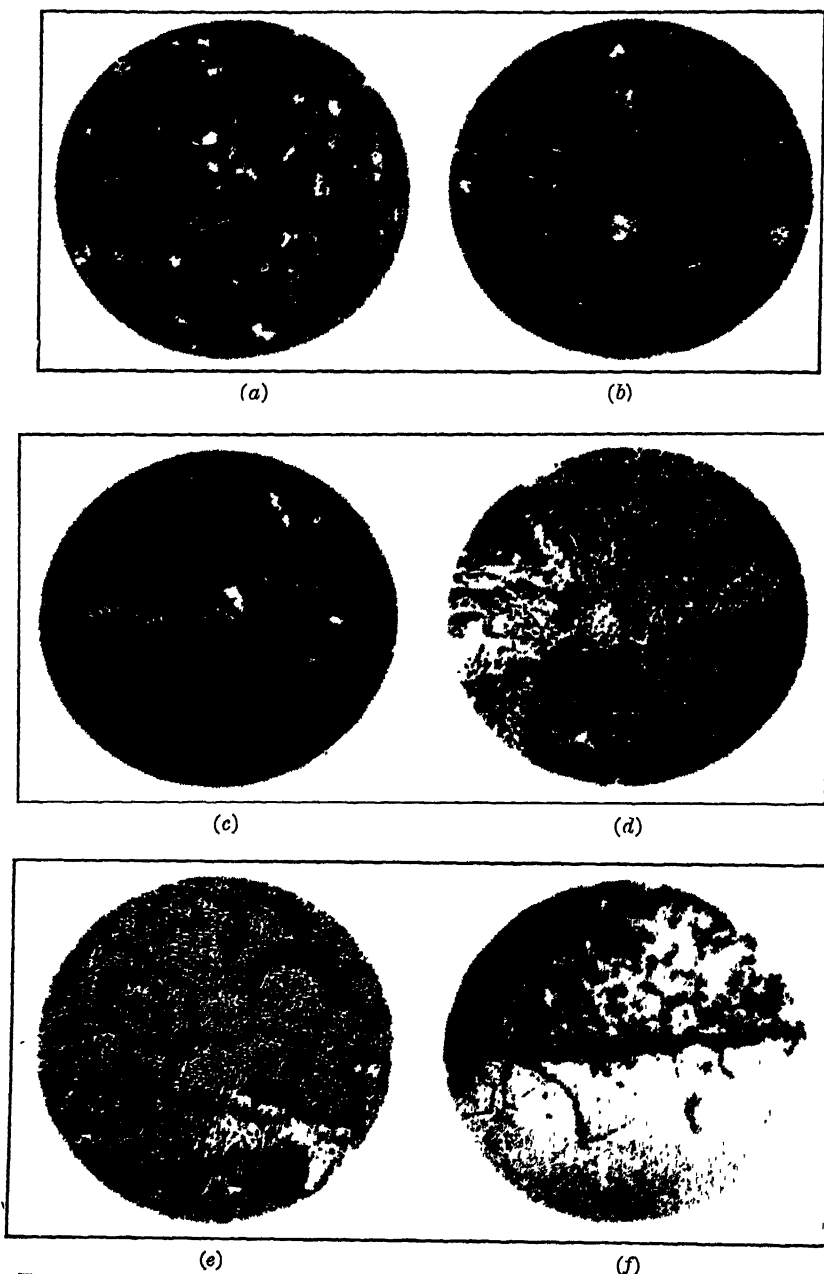


FIG. 4.—MICROSCOPIC ASPECTS OF BRASS CORROSION IN SULFURIC ACID AND MINE WATER; (a) SHEET, GRAIN SIZE 0.25 MM. DIAMETER, CORRODED IN  $H_2SO_4$ , PHOTOGRAPHIC ILL.,  $\times 10$ ; (b) SHEET 0.025 MM., MINE WATER, PHOTOGRAPHIC ILL.,  $\times 10$ ; (c) TUBE, MINE WATER,  $\times 300$ ; (d) SAME AS (c) BUT  $\times 500$ ; (e) SHEET, 0.25 MM.,  $H_2SO_4$ ,  $\times 300$ ; (f) TUBE, 0.100 MM. DIAMETER, MINE WATER, CRACKS ON INNER EDGE, ETCHED  $NH_4OH + H_2O_2$ .  $\times 300$ .

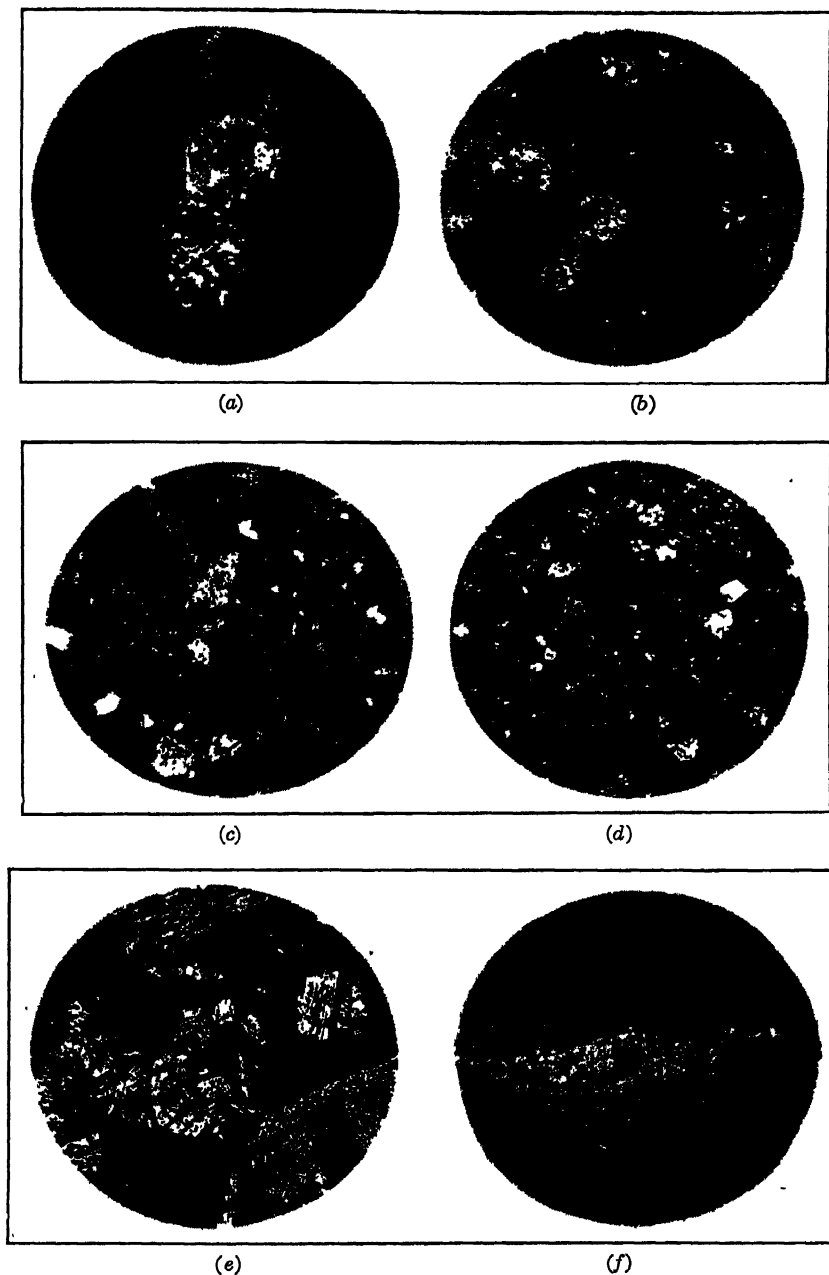
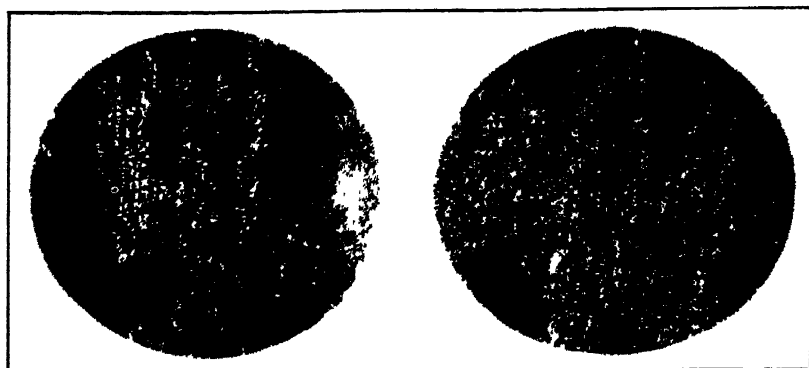
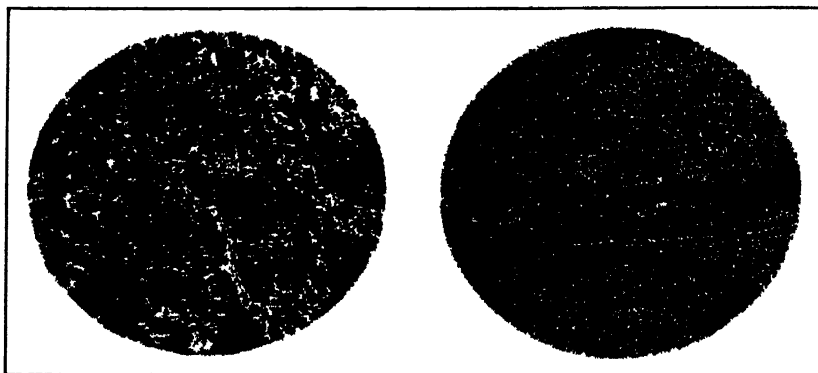


FIG. 5.—MICROSCOPIC ASPECTS OF BRASS CORROSION IN SEA WATER AND SODIUM-CHLORIDE SOLUTION; (a) TUBE, GRAIN SIZE 0.082 MM. DIAMETER, CORRODED IN SEA WATER,  $\times 300$ ; (b) TUBE, 0.030 MM. DIAMETER, SEA WATER,  $\times 300$ ; (c) SHEET, 0.025 MM., SEA WATER,  $\times 10$ ; (d) SHEET, 0.25 MM. SODIUM-CHLORIDE SOLUTION,  $\times 10$ ; (e) SHEET, 0.25 MM. SODIUM-CHLORIDE SOLUTION,  $\times 300$ ; (f) TUBE, 0.030 MM. DIAMETER, SODIUM-CHLORIDE SOLUTION, CRACKS ON INSIDE EDGE, ETCHED  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ ,  $\times 300$ .



(a)

(b)



(c)

(d)



(e)

FIG. 6.—MICROSCOPIC ASPECTS OF BRASS CORROSION IN SODIUM-HYDROXIDE SOLUTION AND TAP WATER; (a) TUBE, GRAIN SIZE 0.100 MM. DIAMETER, CORRODED IN TAP WATER,  $\times 300$ ; (b) TUBE, 0.100 MM. DIAMETER, SODIUM-HYDROXIDE SOLUTION,  $\times 300$ ; (c) SHEET, 0.025 MM. TAP WATER,  $\times 300$ ; (d) SHEET, 0.015 MM., SODIUM-HYDROXIDE SOLUTION,  $\times 300$ ; (e) TUBE, 0.038 MM. DIAMETER, SODIUM-HYDROXIDE SOLUTION, CRACKS AND NODULE OF COPPER, ETCHED  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ .  $\times 500$ .

corroded in sodium-hydroxide solution is shown; the corrosion left parallel ridges and minute pits. In (c) is the microstructure of a sheet sample that was pitted but parallel ridges were not formed. In (d), ridges or nodules resulted from the attack. (e) shows the edge of a tube with a copper nodule, or copper deposited in a pit. The deposited copper layer on the edge may also be noted. Corrosion in the alkaline solutions is characterized by the formation of coatings of copper, or copper oxides and hydroxides, which adhere much more tightly than the coatings formed on samples corroded in the other media. Cracks are set up at the edges of tubes on corrosion in the alkaline solutions as in the other media.

### SUMMARY AND CONCLUSIONS

The following conclusions are drawn as a result of this investigation:

1. The effect of grain size on the corrosion loss of admiralty metal (70:29:1 copper-zinc-tin) in the six solutions tested is very small and probably can be ignored in practice. This refers to grain size within the limits 0.01 to 0.10 mm. diameter.
2. In general, brass with smaller grain size corrodes less than that with larger grain size.
3. The microstructural aspects of the material corroded in similar solutions (*i.e.*, acid, basic, and neutral) are similar.
4. Intergranular cracking is caused by the action of the various corroding media.

### DISCUSSION

HENRY S. RAWDON,\* Washington, D. C. (written discussion).—So numerous and so varied are the factors that affect the corrosion of metals that particular care is necessary in corrosion tests to eliminate so far as possible all extraneous factors. It appears to the writer that the question may well be asked as to whether all the necessary precautions have been observed in this investigation. It may be that the points to be mentioned were considered by the authors and found to be insignificant; however, there is nothing in the report to show this.

It appears to the writer that a sample entirely immersed within the liquid should give more accurate and reproducible results for two reasons. (1) The corroded area can be measured more accurately. Figs. 2 and 3 show that the boundary line between the corroded (immersed) portion and the uncorroded part is decidedly irregular in some cases; hence the measurement of the corroded area is bound to be subject to some error. (2) The elimination of any error caused by the "water line" effect. It is a matter of common experience that a specimen partly immersed within a corrosive liquid is, in practically all cases, attacked most vigor-

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\* Physicist, Bureau of Standards.



ously at the "water line." Specimens totally immersed are free from this relatively more intense localized attack. Whether this factor is of any material importance in corrosion tests of the kind discussed in this particular investigation is not apparent from the report.

The use of totally immersed specimens would necessitate, of course, a slight modification in their preparation. Instead of a simple soldered junction at the top on the outside, a union of the same kind on the inside of the tube, which could then be filled with paraffin or other wax, would be necessary.

It may be pointed out, in passing, that in Fig. 1, the plotted data do not justify the two lower curves being drawn as shown. When drawn as the data suggest, they help to confirm further the general conclusion reached by the authors concerning the relation between the grain size and the corrodibility of brass.

ROBERT J. ANDERSON.—When these tests were carried out the points just mentioned were considered, but it was decided to employ the methods described because we had done previous work in the same way and wanted to carry that along. Subsequently, we have used total immersion tests; in the case of tubing we have inserted a cork in the bottom and applied sealing wax, or similar substance, to the top so that only a portion of the external surface of the tube sample is exposed. Some of the apparent anomalies in the curves may be explained by lack of precision in the method. But in spite of that, the results show, and they have been checked time and time again, that this matter of grain size is apparently not important.

W. R. WEBSTER, Bridgeport, Conn.—In that connection is not the author's statement possibly open to misconception? He states that the corrosion is less in the case of the finer grains than in the case of the coarser; the paper, though, shows that that statement cannot be made very broad.

ROBERT J. ANDERSON.—That is quite true. As I explained, when reading the paper, subsequent work has shown that apparently grain size does not have any effect at all within a range of sizes with which we are concerned.

FRANCIS B. COYLE, Brooklyn, N. Y.—Was an attempt made to standardize the length of time used in making the corrosion test? If a fitting is put in service, a certain amount of corrosion takes place; has any work been done to correlate the amount of corrosion that takes place in the test and the actual corrosion that takes place in service?

ROBERT J. ANDERSON.—Not in the present instance. Work has been done, however, by the Bureau of Mines on the correlation of results

from simple immersion tests in mine waters with results from the accelerated electrolytic corrosion test in the case of about fifty metals and alloys. Simple immersion tests have not been made of the tube samples described in the present paper, nor has correlation been made with service corrosion data.

MR. SAURWEIN.—Do these grain sizes correspond with grain sizes used in commercial tubing specified by the A. S. T. M.?

WILLIAM B. PRICE, Waterbury, Conn.—The grain size was approximately 0.01 to 0.10 mm.; it was within the A. S. T. M. specifications approximately up to 0.045 mm.

W. R. WEBSTER.—It covers the range within which the tubes are likely to be found in service, and a somewhat wider range than is permitted by the A. S. T. M. specifications.

## The Reduction and Refining of Tin in the United States

BY H. H. ALEXANDER,\* AND J. R. STACK,† MAURER, N. J.

(New York Meeting, February, 1924)

PRIOR to 1915, numerous attempts were made to treat tin concentrates in the United States, but for various reasons they were unsuccessful. Tin ore is said to have been found in nearly every state, but none of the deposits has proved to be of commercial importance. An annual output of a few hundred tons in Alaska is the only domestic production; hence any considerable production of tin in the United States must be from foreign ores. The most promising occurrence of tin was found in the Black Hills, S. Dak.; in the early development stage, it was called the Cornwall of America. Associated with the tin is tungsten. The story is told that an exceedingly fine specimen of the Black Hills ore was sent to England to encourage stock promotion; the desired effect was produced until a skeptic chipped off a small piece, which the analysis showed to be wolframite.

### FIRST ATTEMPTS AT SMELTING

One of the first promising attempts at tin smelting in the United States was made by R. T. White at Bayonne, N. J., in 1903. Mr. White, after spending some time in England studying the methods of tin smelting, organized a company called the International Tin Co., and erected a plant to treat tin concentrates from the Straits of Malacca. About the time the plant was completed, the English Government placed an export duty of 40 per cent. ad valorem on tin concentrates exported to other than British smelters, which duty made it impossible to operate this plant so the enterprise was abandoned. As this export duty is still effective, the only source of tin-ore supply for the United States is the Bolivian concentrates.

### BOLIVIAN TIN CONCENTRATES

Unlike the alluvial placer deposits, nearly all Bolivian tin occurs in lode deposits and some of the highest grade ores contain only a small

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percentage of tin. The Bolivian tin concentrates, or "barilla," usually contain from 58 to 70 per cent. of tin, while the concentrates from the alluvial deposits, especially the Straits, contain from 70 to 76 per cent. of tin, the balance being slag-forming constituents. If pure, the mineral cassiterite contains 78.8 per cent. of tin. The tin in Straits concentrates is easily reduced and the resultant metal is of high purity containing from 99.75 to 99.9 per cent. tin; the treatment of the Bolivian concentrates is extremely complicated and to produce a similar grade of tin from Bolivian ores, special extra treatment such as electrolytic refining is necessary.

Some of the impurities generally associated with Bolivian tin ores are:

- (1) Easily reducible impurities—lead, copper, arsenic, antimony, bismuth;
- (2) more difficult to reduce—iron;
- (3) slag-forming—silica, alumina, lime, tungsten;
- (4) matte-forming—sulfur.

Although Bolivian ore-dressing methods have been referred to as crude and defective, in most cases, a good grade of concentrates is produced. Recently, improvements have been made in the product by means of roasting, magnetic separation or lixiviation; in this manner, impurities not easily eliminated otherwise are removed. Concentration by flotation is applicable to tin ores as a number of the impurities—iron, bismuth, lead, copper, etc.—occur as sulfides; the sulfide concentrates contain the impurities and small amounts of tin oxide, while the tailings contain the tin oxide essentially free from impurities. The flotation process has been successfully used for separating lead from tin in the Far East and has recently been introduced in Bolivia.

When the amount of the reducible impurities is small or so related to the tin contents that, on smelting, a metal of merchantable quality can be produced, no preliminary treatment of the concentrates is necessary. Some of the Bolivian concentrates are sufficiently pure for direct smelting for the production of common, standard, or smelter tin, which usually contains 99.00 to 99.30 per cent. tin and is suitable for making solder and some alloys. Lead is not an objectionable impurity for solder making; many brands of Chinese tin contain several per cent. of lead.

Although the Bolivian concentrates can be purified by roasting with chemicals and leaching preliminary to smelting, the metal produced is inferior in purity to Straits, Banka, or Electrolytic tin. The usual impurities associated with tin, such as lead, copper, arsenic, antimony, and bismuth, cannot be eliminated by such simple methods as scorifying, liquating, crystallization, or poling. The series of oxidization of these metals is as follows in the order given: tin, antimony, arsenic, lead, bismuth. To date the only practical solution of the problem for the separation of these impurities from the tin lies in electrolysis, in which case preliminary treatment of the ore before reduction, while desirable, is not necessary.

## REPRESENTATIVE ASSAYS OF TIN CONCENTRATES

	Bolivian												
	Sn, %	Bi, %	Pb, %	Cu, %	SiO <sub>2</sub> , %	Fe, %	CaO, %	Al <sub>2</sub> O <sub>3</sub> , %	S, %	As, %	Sb, %	WO <sub>3</sub> , %	
1	59.2	0.93	0.18	0.12	1.30	5.4	0.50	1.21	3.0	0.00	0.04	0.07	
1a	69.1	0.85	0.23	0.27	1.20	5.1	0.30	1.05	3.0	0.02	0.06	0.08	
1b	68.0	1.55	0.17	0.13	1.90	4.8	0.40	1.30	2.8	0.02	0.03	0.16	
2	57.3	0.08	4.7	0.07	2.80	12.0	0.20	0.60	2.8	0.04	0.15		
3	58.0	0.05	0.15	0.25	2.80	13.5	0.30	1.80	3.0	0.04	0.08		
4	67.0	0.07	0.06	0.80	2.50	5.0	0.50	0.60	0.6	0.02	0.03	0.04	
5	60.7	0.03	0.05	0.07	4.80	6.5	0.40	1.70	2.31	0.03	0.04		
6	53.8	0.03	12.17	0.05	4.16	5.7	0.60	0.99	2.55	0.05	0.04		
7	56.8	0.06	0.55	0.01	2.40	9.6	0.40	1.90	0.80	0.06	0.14		
	Alaskan												
1	60.6	0.07	0.05	4.4	3.0	1.6	2.0	0.03	0.05	0.07			
2	69.0	0.15	0.08	4.1	2.4	0.5	0.25	0.01	0.05	0.05			
3	54.0	0.04	0.02	15.0	6.5	1.0	1.4	0.01	0.01	0.07			

The accompanying tabulation is representative of the various Bolivian brands; such as Araca, Colquiri, General, Huanchaca, Llallagua, Oruro, Oploca, etc., also the product from Alaskan producers, such as the American Tin Dredging Co., Northern Commercial Co., and the York Dredging Co. These analyses are representative of the class of material treated during 1918 to 1922. The concentrates occasionally contain small amounts of gold and silver, but their presence is erratic. Many of the Bolivian tin properties were formerly worked as silver mines but the tin concentrates do not now contain sufficient silver to be considered an asset. It is not uncommon to find gold associated with tin in the Alaskan placer deposits and the miners pay particular attention to its removal.

## PURCHASING OF TIN CONCENTRATES

The purchasing of tin concentrates in this country is done chiefly by contract, usually on an annual basis calling for delivery of a certain definite tonnage.

*Payment for Tin*

Usually 96 to 98 per cent. of the tin contents are accounted for, depending on the kind of ore; in some cases payment for all the tin is made, the smelting losses, etc. being taken care of in the treatment charge. The value of the tin is usually determined by taking the average of the prices ruling on the London Metal Exchange for Spot and Three Months Standard Tin, as quoted during the second calendar month after shipment is made. This means that if a shipment is made on January 14, the liquidation would be made as per the average of the quotations for the month of March.

### *Treatment Charge*

The returning charge and final settlement for the ore is made in pounds sterling. The rate of exchange in recent years has been an important factor in governing the net returning charge; therefore, to offset fluctuations in the rate of exchange and to stabilize the returning charge, the value of the pound sterling may be fixed for the duration of the contract. All transactions are based on a ton of 2240 lb.

### *Premiums and Penalties*

The concentrates are nearly all purchased on a 60 per cent. tin basis; for each unit or fraction thereof above or below 60 per cent., the returning charge is reduced or increased at the rate of 5s. per unit. The net returning charge has varied from £10 to £25. The basic price for standard tin is generally taken at £170 per ton and the returning charge is increased or decreased at a fixed rate for each pound sterling the settlement quotation is above or below £170. One per cent. of sulfur is allowed free and is penalized at the rate of 10s. per unit or fraction thereof over 1 per cent.

### *Iron*

Five per cent. of iron is allowed free and is penalized at the rate of 10s. per unit or fraction thereof over 5 per cent. The usual splitting limit on assays are as follows: Tin 0.5 per cent., sulfur 0.2 per cent., iron 0.2 per cent.

The undesirable constituents such as lead, copper, arsenic, antimony and bismuth are not penalized specifically but an increased treatment charge is made to cover costs occasioned.

### ASSAYS AND ANALYSIS

On tin concentrates, the determination of the settlement assay is always made by the fire-assay method; *i.e.*, fusion with sodium cyanide. The method is unreliable at its best. As most metals are reduced by the cyanide, their removal is necessary before fusion. Many are removed by prolonged treatment of the finely divided sample with HCl and HNO<sub>3</sub>. Iron is difficult to eliminate entirely; and if present as magnetite, it is never completely removed. Tungsten and silver are removed, if present, by treating the residue with NH<sub>4</sub>OH.

Small amounts of tin are retained in the slag. Silica causes incomplete recovery of tin; up to 10 per cent. SiO<sub>2</sub> the error is not large but above this it soon becomes prohibitive. These errors, together with absorption and volatilization, are usually less than the error due to the iron and other impurities reduced with the tin in the button. Correction for purity of the button is not allowed. The cyanide-tin results are always checked by a reliable wet method.

The volumetric analysis is done according to the well-known method of E. V. Pearce. The sample is generally decomposed by fusion with  $\text{Na}_2\text{O}_2$ ,  $\text{NaOH}$ , or by heating with  $\text{CaCO}_3$ . The melt or heat is dissolved in  $\text{HCl}$  and the tin reduced to the "ous" state by metallic nickel in strong  $\text{HCl}$  solution and then titrated with iodine in an atmosphere of  $\text{CO}_2$ . The method is used on ores, slags, and intermediary products.

The determination of tin in metal, such as refined tin and anodes, is made electrolytically by deposition from a double ammonium-oxalate solution. Credit for working out the details of this method are due to Messrs. Eyerluss and Jaeger, of the Perth Amboy plant. The impurities in tin are determined by methods similar to those outlined by W. A. Cowan.<sup>1</sup>

## PRACTICAL TESTS FOR TIN

### *Cornish Assay*

The Cornish assay is made to determine the approximate quantity and quality of the tin that will be produced from smelting a given ore. The sample is fused with 20 to 25 per cent. of fine coal. The button produced is melted in a small iron ladle and the excess tin is removed from the dross or alloy by squeezing with a thick iron spatula. When cool enough, the tin is poured into a sandstone or marble mold and the specimen examined for characteristic appearances.

### *Stone-mold Test*

If a sample test bar of tin is cast by pouring into a stone mold, which allows slow cooling, the segregation of the impurities will be more pronounced for visual examination. If the sample is pure, the surface of the bar will be bright, smooth, lustrous, and slightly convex. Impurities cause a dull, frosted, or crystalline appearance and a rough or depressed surface. To one experienced with the test, it serves as an excellent guide to the quality of the tin under consideration. Small amounts of iron, copper, and arsenic usually increase the surface luster and hardness. Contamination with lead, copper, and bismuth, in small percentages, is indicated by a frosty appearance on the surface.

Arsenic has the most pronounced effect on tin and in quantities over 0.1 per cent. it is very deleterious, causing brittleness and increasing hardness. If present in sufficient amount, the test bar may show a bright lustrous surface similar to pure tin and consequently may hide many other impurities.

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<sup>1</sup> Metallurgy of Tin and Antimony. *Trans. Am. Inst. of Metals* (1914) 8, 196.

*Fracture or Bending Test*

A sample bar of the tin under consideration is poured into a small iron mold and allowed to cool. When cool, it is partly cut through in the center with a sharp chisel, bent double, and the fracture examined. A smooth or silky appearance of the fracture indicates high purity and a broken or ragged fracture shows impurities. The hardness and brittleness are perceptibly increased by small percentages of lead, copper, arsenic, and bismuth and the fracture will break or tear on bending, if any of these impurities are present.

Antimony can be present without positive detection by these tests; if suspected in large amounts, an additional test is made. The sample is mixed with an equal weight of lead and a small solder bar cast, which will show a frosted line in the center if considerable antimony is present.

The same test is used for arsenic. If present in quantities much over 0.1 per cent., the surface of the solder bar will be covered with small circular blotches, the appearance of which is strongly objected to by the solder trade.

*Establishment of Tin Smelting in United States*

In 1915, an opportunity presented itself for the establishment of a tin-smelting industry in the United States. Because of the World War, the Bolivian tin concentrates could not be safely transported to Europe, with the result that large stocks were accumulated and Bolivia, having no smelting facilities, was obliged to look elsewhere for disposal of this large surplus. Her output had gradually increased until it was about 25 per cent. of the world's production. A scarcity of the metal had become noticeable in the United States. The American Smelting & Refining Co., therefore, decided to treat these ores and the Perth Amboy plant at Maurer, N. J., was selected for the smelter site.

Ernest V. Pearce, of Cornwall, England, was secured to design and operate the plant. Plans were drawn and construction started in July, 1915; the new smelter was built and operations were begun in March, 1916. After designing the plant, Mr. Pearce spent several months in Bolivia contracting for an ore supply. Such ores were selected as would, by blending, produce tin of a merchantable quality. Mr. Pearce remained until 1918 and much of the credit for the success of the venture was due to his efforts. In 1918, the Williams Harvey Corp., of England, and the National Lead Co. jointly erected a tin smelter at Jamaica Bay, Long Island, at which plant a leaching process was successfully used, preliminary to smelting for the production of standard tin.

Several other smelters sprang up about this time but did not continue permanently; Richards & Co., at Boston, and the American Tin Smelting Co., at Matawan, N. J., may be mentioned. Also companies producing



white-metal occasionally smelted tin concentrates, such as the Union Smelting & Refining Co., at Newark, and the Nassau Smelting & Refining Co., at Tottenville, Staten Island.

### *Description of Perth Amboy Plant*

The Perth Amboy installation consists of the various buildings with the following equipment:

*Sampling Mill:* Scales, crusher, rolls, sample finishing room, elevators and storage bins.

*Roaster Building:* Two 15-ft. diameter, Wedge, muffle-type roasters.

*Reverberatory Charge Building:* Scales, elevators, pug mill, crusher, screen, rolls and storage bins.

*Reverberatory-furnace Building:* Two oil- or powdered-coal-fired reverberatory furnaces, hearth 12 by 40 ft. equipped with 150-hp., waste-heat boilers.

*Liquator Building:* Three liquating furnaces, two 15-ton cast-iron holding kettles, a 10-ton crane, and an anode casting wheel; in addition, two small reverberatory concentrator furnaces for treating bismuth slimes.

*Blast-furnace Building:* Blast furnace 42 by 144 in. at tuyeres, a Dwight-Lloyd sintering machine, necessary charge scales, and slag-granulating system.

*Slag-furnace Building:* Two reverberatory, slag-settling furnaces 14 by 28 ft. long with slag-granulating system.

The furnace buildings are connected and served by two 24-in. gage, electric, industrial locomotives. The ore to and from the roasters is trammed on an 18-in. industrial track, connecting the roasters, reverberatory charge building, and the sintering machine. All of the smelting furnaces, except the slag-settling furnaces, are connected to a baghouse by a trunk flue.

*Accessory Equipment:* Baghouse, powdered-coal installation, oil storage and equipment, and bedding system.

### PROCESSES AND PURIFICATION

The process intended to be used was the time-honored method practiced in England. Generally speaking, the practice of the art had been maintained a closely guarded secret. It is not a reflection to say that no important changes or advances had been made in the metallurgy of tin for many decades. The process was satisfactory, competition was not sufficient to warrant a change, and the class of concentrates available was not of an exceedingly impure character; or, if so, an ample supply of concentrates free from impurities could be obtained for blending to produce standard tin.

Professor Henry Louis states, in the preface of his book "Metallurgy of Tin:"

Authentic information on the subject of tin smelting is somewhat scarce. The small amount of new matter is due to two reasons, firstly, the unprogressive character of tin smelting which continues from decade to decade with comparatively little change, and secondly, the profound degree of secrecy observed by tin smelters who are extremely anxious to keep to themselves any modifications or improvements in the processes of tin smelting. To what extent those two facts, the slow advance of the industry and those engaged in it, are related as effect and cause, may be left to the judgment of the reader.

It was the intention to give the ores a chloridizing or sulfating roast with subsequent leaching with muriatic or sulfuric acid for the extraction of iron and impurities. The lixiviant could be purified and the iron precipitated, recovered, and marketed as hematite or rouge, and the lixiviated ore reduced to metallic tin. For this purpose, two five-hearth Wedge muffle roasters were installed, one up-draft for the chloridizer and one down-draft for the sulfatizer. The ferriferous ores were to be sulfated by adding sulfur and roasting and the sulfide ores chloridized by adding salt and roasting. The processes of sulfating and chloridizing were patented by E. V. Pearce, from whom rights to use were acquired.

After a complete investigation of the chloridizing and leaching process, it was concluded that it did not offer sufficient advantages. Although the removal of any iron would facilitate the smelting operations, the final metal produced would not command the high price obtained for electrolytic or other pure tin.

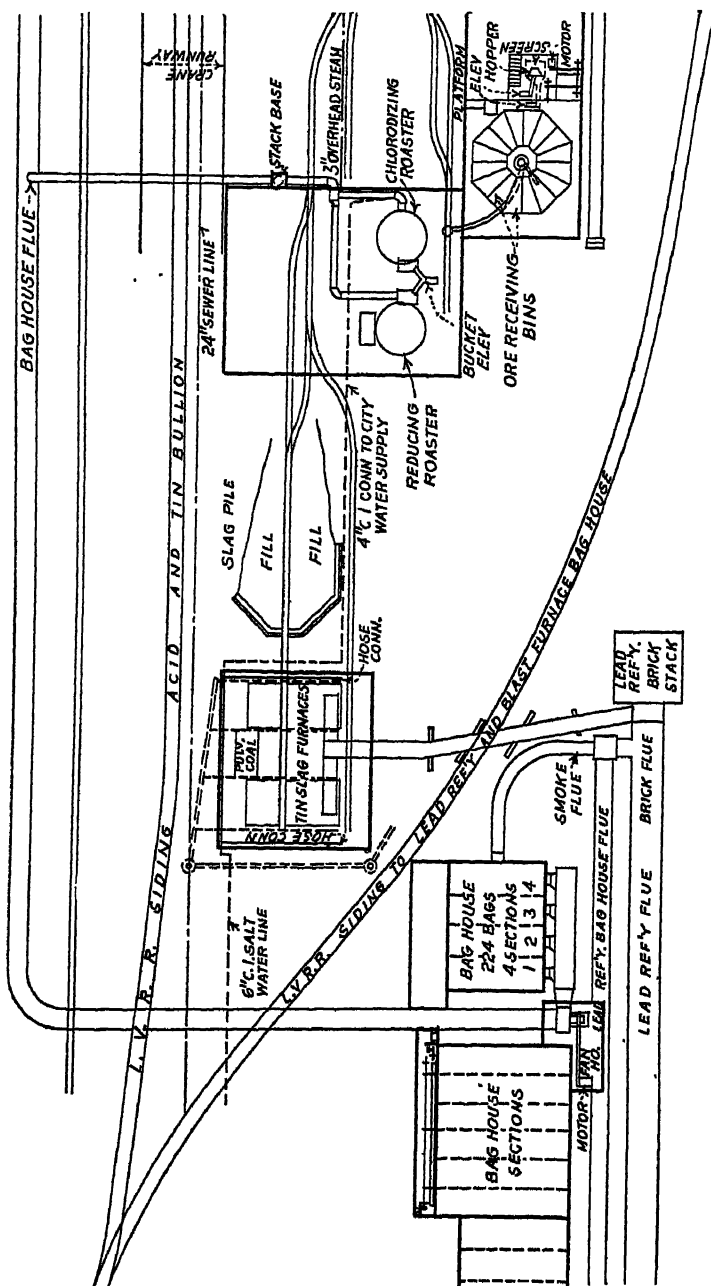
Without going into the details of the process, it will suffice to say that the purpose of this operation of roasting and leaching was to eliminate reducible impurities such as lead, copper, arsenic, antimony, and bismuth, and remove iron and sulfur. The operation is difficult, and a clean, sharp separation of the impurities is not easily made; consequently, the tin produced is not of such high purity as that produced by electrolysis. The elimination of the iron is partial, but whatever is eliminated is advantageous. Many of the tin smelters in England and on the Continent use some method of purification before smelting such as salt roasting and leaching.

### SMELTING PROCESS

Smelting operations were started at the Perth Amboy plant in March, 1916, and the methods and improvements will be described in chronological order.

#### *Receiving and Sampling*

The tin concentrates, as received from Bolivia, are contained in paper-lined jute or canvas bags, each containing 110 lb. of ore. The ore is delivered to the sampling building, where weighing, moisturing, and



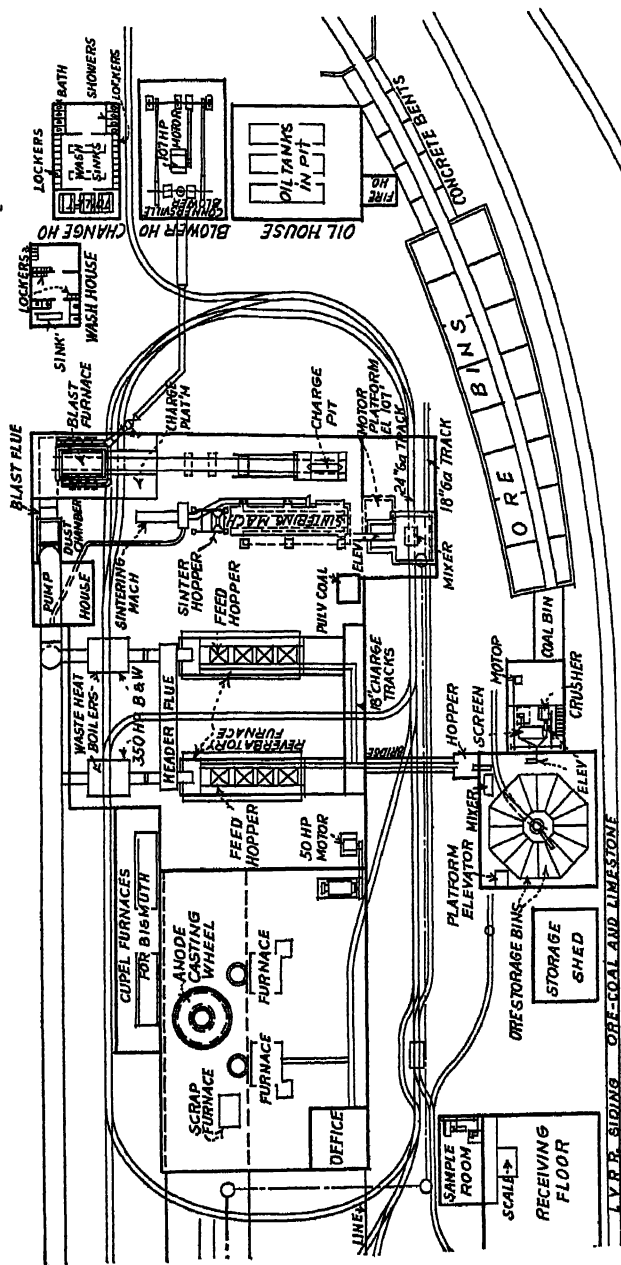


FIG. 1.—LAYOUT OF PLANT.

sampling is done according to conventional methods, in the presence of the shipper's representative. The concentrates classify into:

Fine—20 to 60 mesh; Coarse— $\frac{1}{4}$  in. size; Lump— $\frac{1}{2}$  by 1 in.

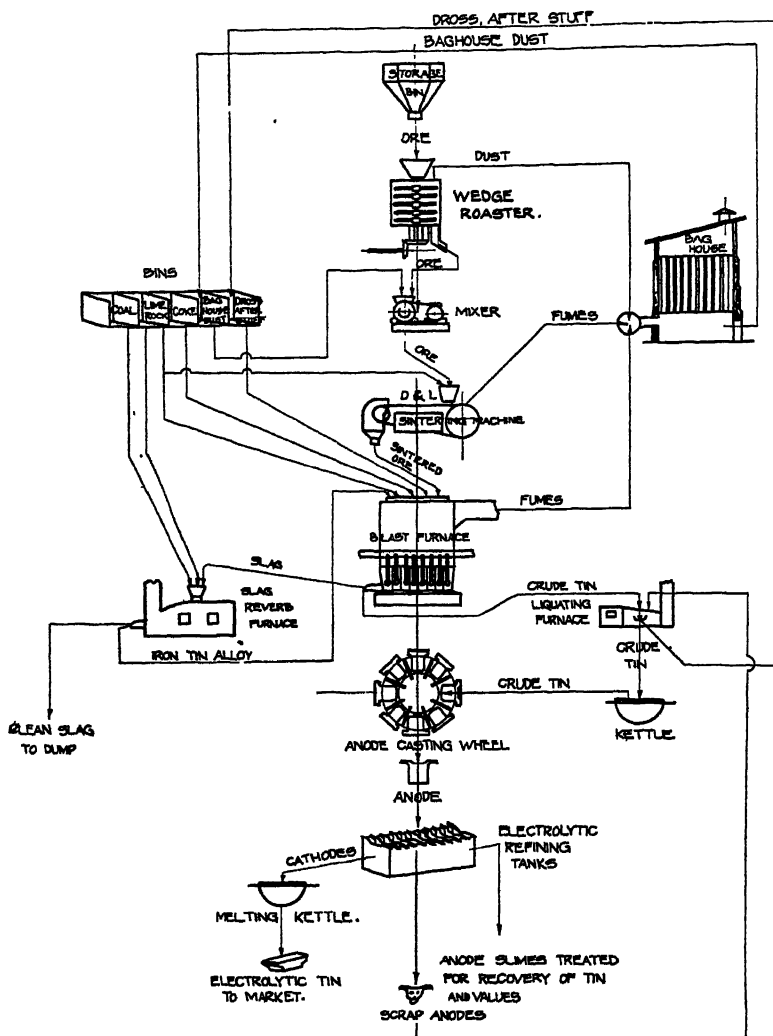


FIG. 2.—FLOW SHEET OF TIN BLAST-FURNACE SMELTING PROCESS.

The bags, when empty, are cleaned by a suction bag-cleaning device, tared, and returned to the shipper. The concentrates are stored in 50-ton bins, where the different grades can be held separately. The lump ore is crushed and rolled to  $\frac{1}{4}$ -in. mesh and is then delivered to bins.

### *Roasting*

The concentrates containing one or more per cent. sulfur are roasted. Any sulfur in the smelting mixture forms tin sulfide, or matte, which is readily volatilized, resulting in heavy tin loss and the production of excessive amounts of byproducts, such as matte, fume, and after-stuff. The roaster charge is from 35 to 40 tons per day and consists, essentially, of ore plus the current amount of byproducts made, such as tin matte, tin fume, and after-stuff (dross from liquating).

The roaster is maintained at a dull red heat, which is sufficient to drive off sulfur. Frequently higher temperatures are obtained through the byproducts, which are often autogenous, because of the sulfides and finely divided particles of tin present.

The roasted material, or calcines, should have the sulfur contents reduced to less than 0.5 per cent. The calcined material is transferred to the reverberatory-charge building storage bins. The hot gases, containing  $\text{SO}_2$ , are conducted to the baghouse and filtered free from dust particles, which are, essentially, finely divided ore.

### *Reverberatory Furnaces*

The two reverberatory furnaces are of the same size, namely 40 ft. long by 12 ft. wide, inside. The arch is built of 12-in. silica blocks and the side walls are built of firebrick, except at the metal line where magnesite bricks are used. The bottom is  $13\frac{1}{2}$ -in. thick, built of firebrick, and is flat except for a slope of 4 in. from the front, bridge, and sides to the tap hole. Particular care and skill are used in laying the bottom, for in spite of the best workmanship, tin will leak through. The bottom is supported by two large I beams longitudinally placed and resting upon brick piers. Upon these I beams are placed transversely 4-in. I beams at 8-in. spacing, and upon the latter are laid rectangular slate slabs about  $\frac{3}{8}$  in. thick, then a 6-in. layer of crushed brick or gravel and fire-clay, on top of which  $13\frac{1}{2}$ -in. brick are laid in header courses. Each brick is either rubbed smooth and laid dry, or else it is dipped in a thin clay wash, closely fitted, and each row keyed as tightly as possible.

The life of a furnace bottom is usually 8 to 12 months. The furnace bottom on slag smelting will last several times longer on account of the refractory nature of the alloy produced, which saturates and builds up on the bottom. A new furnace bottom is seasoned by alternate heating and cooling with an abundance of alloy, until it has become saturated; this is the safest and best method to prevent the bottom from excessive leaking.

Each furnace is equipped to be fired either by powdered coal or oil; the change from one to the other can be made on a moment's notice. The use of powdered coal is preferred to oil or hand

firing and no particular difficulties are encountered with its use, except the accumulation of ash in the uptake; this is remedied by increasing the area of the uptake and by frequent cleaning.

A deep concrete vault is built under each furnace in order to collect the tin that leaks through. The slates underneath the bottom are pricked, when a new bottom is first started, to allow drainage for the tin that will leak through so as not to risk raising or jumping the bottom. The furnace bottom is cooled by natural draft through the vault and the temperature of the vault is not high enough to maintain the tin that has leaked through in a molten condition. Periodically, the tin is removed by specially heating the vault.

### *Reverberatory Smelting*

The roasted material, consisting of concentrates and byproducts containing generally 60 per cent. of tin or better, is thoroughly mixed with fine anthracite as a reducing agent. About 20 to 30 per cent. of coal is used for reducer, depending on the fineness of the roast and the fixed carbon or reducing power of the coal. The necessary fluxes are added to the mixture to give the desired slag; to ferriferous ores, silica may be added. The addition of silica increases the amount of slag produced and is not ordinarily used, unless ores high in iron are encountered. The charges are carefully made up in order to reduce the tin and produce a slag of about 35 per cent.  $\text{SiO}_2$ , 12 per cent. Fe, 25 per cent.  $\text{CaO}$ ; this is the composition of the so-called clean, or waste slag, which contains about  $1\frac{1}{2}$  per cent. of tin.

When smelting concentrates low in iron, a complete reduction of the tin is made in one operation and the clean slag is thrown away. On ores containing 3 per cent. or more iron, a two-stage smelting operation is necessary, in order to separate iron from tin. In the first step, 85 to 90 per cent. of the tin is reduced, the remainder going into the slag together with the iron. This slag is then resmelted to reduce the balance of the tin; to accomplish this, part of the iron must also be reduced. The tin and iron reduced unite to form an alloy. The separation of the tin from iron in this alloy has been the bane of tin smelting. The smelting of tin concentrates containing iron can be divided into two steps, ore smelting and slag smelting.

### *Ore Smelting*

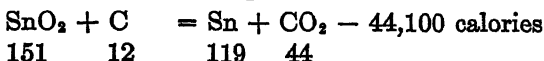
After the roasted material has received its fluxes and is thoroughly mixed, the charge containing 12 to 15 tons of ore is delivered to four steel charge hoppers located centrally over the furnace. When the furnace is empty, from the previous charge, the heat is diminished and the next charge is dropped from the hoppers and spread over the furnace bottom. The heat is raised and for the first 4 to 6 hr. the charge is not disturbed.

As soon as fusion begins and the charge starts to become pasty, it is stirred at  $\frac{1}{2}$ -hr. intervals through the four side doors with long iron rabblers. The time consumed in smelting a charge varies from 10 to 12 hr. Fusion is complete when the charge becomes quiet and no dirty material comes off the bottom when stirred; the furnace is then ready to be tapped. The temperature of the furnace is maintained in the final smelting period at about 1300° C. The reduction of tin is a highly endothermic reaction and a perceptible increase in the temperature of the furnace occurs after the reaction is completed.

Based upon thermo data taken from "Metallurgical Calculations" by Richards, the following is derived:

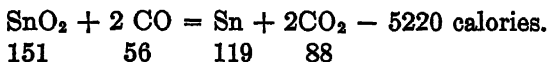
1.  $\text{SnO}_2 = \text{Sn} + \text{O}_2 - 141,300$  calories
2.  $\text{C} + \text{O}_2 = \text{CO}_2 + 97,200$  calories
3.  $2\text{CO} + \text{O}_2 = 2\text{CO}_2 + 136,080$  calories

Adding equations (1) and (2) gives:



which means that the reaction consumes 44,100 calories and therefore is heat, which must be supplied from an extraneous source. It is equivalent to 371 calories per unit of tin, or 667 B.t.u. per lb. of tin.

Adding equations (1) and (3) gives:



which means that the reaction consumes 5220 calories and therefore is heat that must be supplied from an extraneous source. It is equivalent to 44 calories per unit of tin or 79 B.t.u. per lb. of tin.

The tap hole is located on the side about midway of the furnace and delivers into a brick-lined settler. The tin is held in the settler and the slag overflows into slag pots. Electric locomotives convey the slag to a pit, where it is granulated. In this form the slag is more easily handled and more suitable for resmelting than if it is poured in layers on plates or beds.

The tin is tapped from the settler into a cast-iron pot and transferred to a holding kettle, from which it is cast into anodes on the usual mechanical casting wheel.

If the tin produced from this smelting is of sufficient purity to be of merchantable quality, it can be cast into bars and sold as common, or smelter tin. In this case, the molten tin is first cast into slabs, which are charged into a liquating furnace and melted slowly at a low temperature and cast into bars. This liquating operation eliminates iron, sulfur, and some arsenic and antimony, as these metals produce alloys having a higher melting point than tin; the lead, copper, bismuth, and metals



forming alloys with a lower melting point than tin are not eliminated. An appreciable amount of tin is converted to oxide and remains in the furnace as dross, together with the impurities eliminated. This dross is the so-called after-stuff.

When common or smelter tin is to be made, only selected ores low in impurities can be used. In making smelter tin, even from selected Bolivian ores unless they are very pure, care must be taken that too much tin is not allowed to enter the slag, or the product will be too impure because of contamination by the more easily reducible impurities in the molten bath. Advantage has been taken of this property in a method for producing pure tin from impure ores, called the partial reduction process.

### *Slag Smelting*

The slag should be worked up as made, by resmelting in a reverberatory furnace. The granulated slag from the ore smelting is mixed with fine coal in sufficient quantity to reduce the tin contained to metal; the proper amount of finely crushed lime rock is added to give a fluid slag. The amount of reducing agent varies from 10 to 20 per cent., by weight, of the slag, depending on the amount of tin to be reduced. The size of the charge is about 10 tons of slag with the necessary amount of coal and lime rock. The time required to complete the furnace cycle is 12 hr. When the furnace is tapped, the slag should be clean, containing not over 2 per cent., and usually run  $1\frac{1}{2}$  per cent. tin. This slag is discarded.

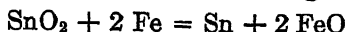
The slag charged, containing, say 10 per cent. of tin and 15 per cent. of iron, has been changed to a slag containing  $1\frac{1}{2}$  per cent. of tin and 12 per cent. of iron and weighs about the same as the original slag; that is, about 85 per cent. of the tin and 20 per cent. of the iron contents have been reduced. Very little, if any, metallic or elemental tin is produced; it is all combined with iron in an iron-tin alloy. This alloy has a higher melting point than tin, depending on the percentages of iron. In this instance, the alloy would contain about 25 per cent. iron and 75 per cent. tin.

The alloy, having a melting point between 1000 and 1200° C., soon becomes thick and mushy at the temperature in the settler and is difficult to handle; it is generally kept stirred in the settler until it cools. In this case, it becomes friable and breaks up, for the most part, into a granular condition similar in size to sand. When it is in the molten state, it can be readily granulated if the stream of metal is broken up with an air blast before striking the water. In either condition, it is in good shape to be handled in subsequent smelting operations.

### *Alloy Smelting*

The iron-tin alloy produced from slag smelting is treated separately for the recovery of tin. By fire methods, this alloy can be decomposed

only by oxidation of the iron. This is accomplished by fusing the alloy with cassiterite according to the following reactions:



Silica, in the form of sand, or crushed brick from old furnace bottoms containing absorbed tin, is added to unite with the iron oxide formed.

The granular or shotted alloy is mixed with the calculated amount of tin concentrates to oxidize the iron contained and the requisite silica-bearing material is added to unite with the FeO formed to produce a slag of the desired composition. The charge, which consists of 10 tons of alloy and the necessary amount of ore and flux, smelts easily and rapidly; the smelting cycle is made in 6 to 8 hours.

The charge should be so fluxed that all of the alloy is decomposed, otherwise great difficulty is experienced in handling the alloy with the heavy fall of metal from this charge.

The slag formed is very liquid and corrosive and hence attacks the furnace walls. On this account, also because of the large tin fall, the furnace should be tapped as soon as ready or danger of jumping the bottom will ensue. In fact, this can be said of all tin charges, but the danger is much greater with alloy charges.

The slag produced is granulated, as usual, and mixed with slags produced from ore smelting for further treatment. There is a run around of iron of about 20 to 30 per cent., 70 to 80 per cent. having been eliminated from the process in the clean slag from the prior slag-smelting operation.

The tin from the alloy charges is usually cast into anodes for electrolysis, its purity depending on the grade and purity of the ore used in the reaction.

To secure complete oxidation of the iron, and prevent alloy production, an excess of  $\text{SnO}_2$  is used and the resultant slag is high in tin. For some unknown reason, the slags are always high in tin whether alloy is produced or not. Theoretically, if an insufficient amount of  $\text{SnO}_2$  has been used and alloy is not decomposed, one would expect the slag to be low in tin. The tin present in the slag is in the form of stannous silicate and tin slags are commonly cleaned by treating with iron. The slags from the alloy treatment usually contain from 15 to 30 per cent. of tin, a typical analysis being:  $\text{SiO}_2$ , 25 per cent.,  $\text{Al}_2\text{O}_3$ , 6.0 per cent.  $\text{FeO}$ , 35.0, per cent.,  $\text{CaO}$ , 1.0 per cent.,  $\text{Sn}$ , 25.0 per cent.

#### CLEANING SLAGS AND ALLOY TREATMENT

Methods for treating the Fe-Sn alloy with  $\text{SnO}_2$  to produce clean slags low in tin and high in iron offer the same fertile field for investigation as does the initial smelting of the ore. It has not been definitely determined whether the tin in the slag is due to insufficient temperature, composition of the slag, or the solubility of iron-tin compounds in the slag.

In alloy treatment, the tin contents of the slag have been reduced to 8 to 10 per cent. and occasionally lower, by replacement with lime and the simultaneous reduction of the tin oxide thus liberated by admixture of carbon. This action has been the basis of an improved process which is later described.

Experiments have shown that if the iron-tin alloy is treated with galena in calculated quantity in excess of the amount required according to the following reaction



the resultant fusion will form a lead-iron matte low in tin and a lead-tin alloy suitable for making solder. Although this method has not been used commercially, the principle has been used in cleaning slags in shaft-furnace smelting. In this instance, the slag containing 10.0 to 20.0 per cent. of tin is mixed with lead oxide, or equivalent lead compounds, and lime rock, and smelted. Sufficient sulfur is present in the charge to form matte, which because of the strong reducing condition, is essentially an iron matte. The slag is more readily cleaned from tin than if lead were not used and the true tin alloy is not precipitated. The slags contain 2 per cent. of tin or under and are nearly always free from lead. The metal produced, white or solder metal, is an alloy of lead and tin of good merchantable quality suitable for solder making. The best results have been obtained by cleaning tin slags by this method, when the composition of the white metal produced contained more than 50 per cent. of lead.

#### CLEANING TIN SLAGS WITH LEAD

A blast-furnace campaign was made in 1917, for cleaning tin slags with lead oxide to produce solder metal. Tin slags of the composition 30 per cent.  $\text{SiO}_2$ , 15.3 per cent. Fe, 20.5 per cent.  $\text{CaO}$ , and 15 per cent. Sn were smelted with lead oxide (litharge) containing 92 per cent. Pb and 0.20 per cent. Sb. Sufficient lead was used to produce a solder metal containing 60 per cent. Pb and 40 per cent. Sn. This proportion gave better results in cleaning the slags than when a 50-50 metal was made.

About 2100 lb. of slag was calculated to be formed containing 30.2 per cent.  $\text{SiO}_2$ , 15.0 per cent. Fe, 25.6 per cent.  $\text{CaO}$ , and 2 per cent. of tin allowed. The average slag from this run analyzed 30.8 per cent.  $\text{SiO}_2$ , 15.5 per cent. Fe, 24.3 per cent.  $\text{CaO}$ , and 2 per cent. Sn. Occasionally, the slags would jump from 1.5 to 3 per cent. Sn without warning but by regular charging and careful regulation of the blast, a uniform slag was obtained. A sample from each slag pot was taken and analyzed for tin, the slags going above 2 per cent. Sn were returned to the furnace for resmelting and those going 2 per cent. Sn or under were thrown away.

Two byproducts were made, fume and matte. Matte containing about 40 per cent. of lead and 30 per cent. of tin was returned to the

furnace charge. A high-iron leady matte containing from 10 to 15 per cent. of tin was discarded from the tin operations. The solder metal, after being melted and drossed, was molded into 100-lb. bars, care being taken to keep the molten solder agitated while molding to insure a uniform

MATERIAL	WEIGHT POUNDS	CHARGE SHEET									
		SiO <sub>2</sub>		Fe <sub>i</sub>		CaO		Sn		Pb	
		PER CENT.	LB.	PER CENT.	LB.	PER CENT.	LB.	PER CENT.	LB.	PER CENT.	LB.
Tin slag.....	2000	30.0	600	15.3	306	20.5	410	15	300		
Refinery oxide.....	420									92	386
Lime rock.....	270	2	5			47	127				
Total.....	2690										
Coke 16.7 per cent....	450										
Coke ash.....	67	45	30	15	10						
			635		316		537		300		386
Slag formed.....	2,100	30.2		15.0		25.6					
Solder metal formed..	642							40		60	

product. The solder metal obtained was of excellent quality and if the trade prejudice were overcome for the metal, this would prove a desirable method of cleaning tin slags. The best grade of solder is made by using equal parts of pure tin and pure lead with the addition of about 0.15 per cent. antimony, making the so-called half-and-half solder.

### BAGHOUSE

Tin readily gives off fumes at a dull red heat, especially when a current of hot gases passes over the surface of the metal, and provisions are made to collect the fumes. All the furnaces are connected to a steel balloon flue, 40 sq. ft. in transverse area, through which the gases are conducted to the baghouse for filtration. The gases from the reverberatory furnaces are cooled by passing through waste-heat boilers and are further cooled by radiation from the balloon flue, which is 700 ft. long, before entering the baghouse. If the temperature of the gases entering the baghouse exceeds 220° F. injury to the woolen bags will result.

The baghouse is constructed according to the conventional design for lead smelting. The present baghouse consists of ten compartments, containing a total of 1000 woolen bags. These bags are 30 ft. long and 18 in. in diameter, giving a total filtering surface of 141,000 sq. ft., or 42 30 sq. ft. per ton-day tin output capacity.

Volatilization of tin is increased by the presence of sulfur. About 2½ to 5 per cent. of the tin contents is volatilized and caught in the baghouse. This fume contains 50 to 60 per cent. of tin in the form of stannic oxide. When the compartments are first opened, the color of the fume is dark gray because of unburned carbon; it burns in contact with air and becomes white and dense. The fume contains small amounts of

lead bismuth, arsenic, antimony, iron, etc. and generally sufficient sulfur to require roasting. Periodically, the dust is removed and added to the roaster charge.

If it were not that some iron from the furnace charge is mechanically carried over into the baghouse, this material could be utilized in the ceramic industry as a base for tin-white enamels. The fume, even after roasting and prolonged treatment by leaching with acids, still contains too much iron to be suitable for such use.

### BYPRODUCTS

Besides slag, there is also formed in tin smelting per ton of ore about 20 per cent. of byproducts; as follows: fume 3 to 6 per cent., matte 2 to 4 per cent., after-stuff 3 to 6 per cent., alloy 8 to 10 per cent. The byproducts, although voluminous, are not particularly difficult to handle, but should be worked up currently. The fume, matte, and after-stuff are added, in the ratio of their production, to the roaster charge. The matte and after-stuff are crushed, rolled, and screened to pass  $\frac{1}{4}$ -in. mesh before roasting.

### AMERICAN MODIFICATIONS IN TIN SMELTING

Soon after operations were started, it was realized that modifications must be made to obtain quantity production and treat byproducts as produced by a continuous process. Experiments were begun with this end in view and, as a result, the blast-furnace process was adopted.

Extensive experiments were made to purify the concentrates before smelting. Leaching with ferric chloride and fusion with niter cake offered some promise but the best results were obtained by tabling, flotation, magnetic separation, or a combination of them. These tests produced two classes of material, one high in tin and low in impurities and one low in tin and high in impurities—a comparatively pure product and an impure one. The first, approximately 80 per cent. by weight of the original ore, recovered about 85 per cent. of the tin in a product assaying about 95 per cent.  $\text{SnO}_2$ . The second contained the balance of the tin, about 75 to 90 per cent. of the iron and 60 to 75 per cent. of the reducible impurities present in the original concentrates.

None of the methods gave a product sufficiently pure to produce a high-grade metal or an impure material sufficiently low in tin to discard. Of course there would have ensued advantages in smelting but the impurities and the iron were still in a product containing tin, which also would have to be smelted. As the electrolytic refining process readily eliminated and recovered the impurities, the segregation of the iron by this treatment did not warrant its installation, although this process might have proved highly beneficial in the original concentration of the

ore at the mines. Magnetic removal of iron is practiced at, at least, one of the Bolivian tin concentrating plants.

Early in 1917, an experimental blast-furnace run was made. The furnace used was a small twelve-tuyere blast furnace 96 by 36 in. at the tuyere level. The tin ore was agglomerated on a standard Dwight-Lloyd sintering machine, to render it suitable for blast-furnace smelting. Smelting was done in two stages, ore smelting and slag smelting by short campaigns on each. The alloy produced from slag smelting was returned to the furnace and decomposed on the ore-smelting charge. Over 1500 tons of tin concentrates were sintered, smelted, and the byproducts completely worked. The results were gratifying and because of the urgent demand for the metal, a Dwight-Lloyd sintering machine and a larger blast furnace were built as an addition to the tin department. The experimental run indicated that a deep column must be used to prevent a hot top, with consequent high volatilization of tin as fume. The furnace started operations Nov. 15, 1917. This innovation in the smelting process has been protected by a series of patents<sup>2</sup> covering sintering, blast-furnace smelting, slag-treatment furnaces, and the production and utilization of tin-iron alloy, which constitutes a continuous process for the whole smelting operation.

### ROASTING AND SINTERING

Serious explosions have occurred in the flues and baghouse, due to the elemental sulfur from the pyrites contained in the sinter charge; consequently, the concentrates are roasted before sintering if they contain any appreciable amount. The sinter charges consist of raw or preroasted concentrates and roasted byproducts; some granulated tin slag for binder and 2 to 3 per cent. of fine anthracite as fuel, together with flux, are mixed with 5 to 6 per cent. of water before sintering.

It is optional whether the silica is added to the sinter charge or to the blast-furnace charge. However, it is expedient to add the lime rock to the sinter charge for the purpose of protecting the grate bars and also for fluxing the sulfur. Calcium compounds, such as  $\text{CaS}$ ,  $\text{CaSO}_4$ , will be largely eliminated in the blast-furnace slag as calcium sulfide, and the matte formation greatly reduced. With raw ore and preroasted byproducts, several campaigns have been made with no matte production. No metallic tin is found in the sinter product nor is much fume evolved.

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<sup>2</sup> H. H. Alexander: Process of Forming Tin Sinter. U. S. Pat. Ser. 419473 (1920); Process of Forming Iron-tin Alloy. U. S. Pat. Ser. 419474 (1920); Process of Blasting Tin Alloy. U. S. Pat. Ser. 419475 (1920); Process of Recovering Occluded Tin. U. S. Pat. Ser. 419476 (1920); Process for Recovering Tin. U. S. Pat. Ser. 1426341 (1922); Process for Recovering Tin from Sulfur Ores. U. S. Pat. Ser. 1461957 (1922).

If any tin is reduced to metal on the Dwight-Lloyd machine, it is re-oxidized before leaving the machine. The sinter is discharged over a grizzly, the fines that pass through the grizzly are returned and the coarse sinter is delivered to the blast furnace.

### BLAST FURNACE

The blast furnace is of the conventional water-jacketed type with mechanical feeding. The dimensions at the tuyeres are 42 by 144 in. The height from crucible to top is 30 ft. The ore column from tuyeres to top of charge is 25 ft. The water jackets are 6 ft. high and are made of steel. The furnace is fed by a 100 cu. ft. car. When charging, both doors on the bottom of the charge car are simultaneously opened and the



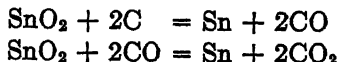
FIG. 3.—TIN BLAST FURNACE.

contents of the car are dropped on to an inverted V-shaped spreader, which serves to distribute the charge properly. The apex of the spreader is located 1 ft. below the top plate of furnace and the charge column is carried to within 6 ft. from the top.

The blast is supplied by a No. 7 Root blower driven by a 85-kw. motor delivering 5500 cu. ft. of air per minute to the tuyeres. The charge column is carried 22 ft. above the tuyeres. The blast pressure is usually maintained between 32 and 38 oz. The normal rate of smelting is about 135 tons of charge per day.

*Blast-furnace Smelting*

The object of blast-furnace smelting is to reduce tin, decompose alloy, and slag iron. The reduction of tin is assumed to occur according to the following reactions:



It would be a comparatively simple matter if the ore contained only tin and easily reducible impurities, but in all the Bolivian tin concentrates that we have received, both iron and tin occur simultaneously. Both are reducible under somewhat similar conditions and, when reduced, unite to form the refractory alloy. The blast-furnace smelting must be so conducted as to make a separation of tin from iron. This alloy of iron and tin is often referred to as "hard head." The real hard head is formed by strong reduction when arsenic is present. It is composed essentially of arsenic, iron, and tin and is very similar in appearance and texture to nickel-iron speiss. Our experience is that the formation of the real hard head is the exception rather than the rule, as it has been noted only on rare occasions.

The blast-furnace charge, consisting of sinter from the Dwight-Lloyd machine, flux, alloy, returned slag, and coke, is spread and mixed in the proper proportions in the charge car. The iron-tin alloy, which is produced from the subsequent slag treatment, is added to the charge to reduce tin according to the reaction



and replaces its equivalent of coke, within limits. That is, with sufficient coke present to furnish the necessary heat for the formation temperatures of the slag and hold the products molten, the iron can practically replace its equivalent weight of coke as a reducing agent, thus making the smelting operation continuous and effecting other economies.

No attempt will be made to explain the reactions that might occur in the blast furnace in the reduction of tin and its separation from iron. It will suffice to say that the reduction and separation from iron is controlled by three principal factors; that is, the degree of reduction, the volume and composition of the slag, and the saturation point of the slag in iron. The saturation point of the slag in iron is taken, for practical purposes, at 20 per cent. iron. This is an arbitrary figure, because it is as high a percentage of iron as we have been able to produce in making finished slags and at the same time maintain its tin contents at about 2 per cent. or less. The practice at other smelters is not generally known. Starting, in 1915, at 10 per cent. iron, the finished slags have been gradually increased until they contain 20 per cent. iron, which we now consider the maximum practical point.



Too much attention cannot be given to the proper preparation of the charge and its distribution in the furnace. With mechanical feeding, the successful operation of the furnace is dependent on these two factors. The sinter product must be a lumpy porous mass free from fines.

It has been found that the blast furnace works well when the larger pieces of the charge are not more than 4 to 6 in.; about, but not much more than, 25 per cent. of the charge should be smaller than  $\frac{1}{2}$  in. Small size charges facilitate better mixing in the blast furnace and usually 2000 lb. constitute one charge. Each kind of material on the charge is spread evenly over the entire surface.

The blast furnace is operated similarly to lead furnaces, except that no side tap or forehearth is used, as the crucible builds up with alloy. The metal and slag are tapped from the furnace through the same opening and delivered into a cast-iron overflow pot, in which the metal is separated from the slag. When the overflow pot is nearly full of tin, it is removed and conveyed to the liquator building and its contents delivered to a holding kettle, from which it is cast into anodes. Just as in reverberatory smelting, the purity of the tin depends on the grade and purity of the ore used, degree of reduction, and amount of slag produced. The slag will usually contain from 5 to 7 per cent. of tin and occasionally as high as 10 per cent. It is sent to the slag-settling furnaces as produced for further treatment.

### *Tin Blast-furnace Slags*

The smelting of ferriferous tin ores in the blast furnace is neither analogous to lead nor iron smelting, but a compromise between the two. The bisilicate slag has given the best results for the production of slags low in tin. Experience has shown that with low-silica, high-lime slags, the tin contents are invariably higher than with those having high silica contents.

A slag of the following composition has proved satisfactory:

	PER CENT.		PER CENT.
SiO <sub>2</sub> .....	37.0	Al <sub>2</sub> O <sub>3</sub> .....	12.0
FeO.....	23.4	MgO.....	3.0
CaO.....	23.0		
Silicate degree:			
SiO <sub>2</sub> .....	37.0 × 53.5% = 19.72		
Al <sub>2</sub> O <sub>3</sub> .....	12.0 × 47.0% = 5.64		
<hr/>			
25.36% oxygen in acids			
FeO.....	23.4 × 22.2% = 5.2%		
CaO.....	23.0 × 28.6% = 6.6%		
MgO.....	3.0 × 40.0% = 1.2%		
<hr/>			
13.0% oxygen in bases			

Ratio  $\frac{25.36}{13.0} = 1.95$ , which corresponds closely to the bisilicate.

This slag fulfills the necessary requirements for tin smelting in that it has a viscosity sufficiently low to allow proper settling of the tin and has a melting point high enough for the tin to be reduced. Much remains to be done in determining the proper furnace conditions and slag composition, to reduce tin selectively and to eliminate the iron in a high-iron slag and thus avoid the production of alloy. By sufficient dilution of the slags with silica and lime, this separation is approached but it is not economical on account of the large amount of slag produced, entailing excessive tin losses. Many fluxes and slag compositions have been tried without improvement.

In the reverberatory process, when first started according to the English method, the iron was eliminated in a clean slag containing 10 to 12 per cent. of iron. In the blast-furnace process, the iron is eliminated in a clean slag containing from 6 to 8 per cent. more iron; therefore, considerably less slag is produced per ton of concentrates.

The tin concentrates from Bolivia are usually too deficient in silica and lime to be self fluxing. With concentrates low in iron, no dilution of the slag with silica is necessary. Lime rock is added to flux the  $\text{SiO}_2$  in the ash from the coal and the small amount in the ore.

The prime requisite in tin smelting is to keep the percentage of slag produced per ton of concentrates as low as possible in order to reduce the losses due to tin being unavoidably carried away in slag. Tin combined in slag is more difficult to reduce than in the concentrates.

The hot ascending gases, containing carbon monoxide, react with the  $\text{SnO}_2$  from the sintered ore, causing a reduction of tin to metal while the tin combined in slag is not appreciably affected by CO and must be reduced by direct contact with carbon at the high temperature of the smelting zone. With concentrates containing

5 per cent. iron, 0.31 ton of slag is made per ton of concentrates.

8 per cent. iron, 0.50 ton of slag is made per ton of concentrates.

10 per cent. iron, 0.62 ton of slag is made per ton of concentrates.

12 per cent. iron, 0.75 ton of slag is made per ton of concentrates.

16 per cent. iron, 1.00 ton of slag is made per ton of concentrates.

20 per cent. iron, 1.25 ton of slag is made per ton of concentrates.

This tabulation is based on the assumption that the finished slag will contain 16 per cent. of iron and correspondingly smaller percentages of slag will be made as the iron contents of the slag is increased. A slag fall of between 50 and 60 per cent. is necessary and is maintained by circulating slag.

#### SLAG-SETTLING FURNACES

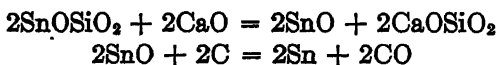
The molten slag from the blast furnace is delivered to the slag-settling furnaces. The slag is poured into a chute, or hopper, which delivers to

the charge hole. The latter is located in the center of the arch and is protected by a water-cooled ring jacket.

The hearth dimensions of the two hot-slag furnaces are 14 by 28 ft. They are similar in design to the ore-smelting reverberatory furnaces, except that there is no vault under the bottom. It is built on a solid concrete foundation and the bottom is laid as an inverted arch with 13½-in. firebricks at a 6-in. slope to front of furnace. Two tap holes are located in the front end, a slotted tap at the slag level, and a water-cooled cast-iron tap jacket at the level of the bottom of the furnace for the metal outlet. The bridge and side walls of these furnaces are cooled at the slag level by circulating water through a 2½-in. iron pipe inserted in the walls. The furnaces are equipped to burn powdered coal or oil. The flow of both coal and air can be adjusted by dampers or by varying the motor speed to get the proper mixture.

The furnaces for slag treatment are an important adjunct to the process because by treating the hot slag the heat required to resmelt the slag is saved, much manual labor is dispensed with and many economies are effected over the former method of smelting cold slag. The temperature of the slag charged is between 1100° and 1200° C. and it is brought up to about 1300° C. These furnaces, besides reducing the tin chemically combined, permit the tin in the form of prills or finely divided shot to settle.

The furnaces are operated as follows: When charged with molten slag, carbonaceous material, usually small sized anthracite, together with finely divided lime rock is added to the bath and rapidly stirred in. The lime replaces the stannous oxide from its combination with silica and the SnO is simultaneously reduced by carbon from the anthracite.



Several additions of the flux mixture (fine coal and lime rock) are necessary to finish a charge. After each addition has been absorbed, a sample is taken from the bath and analyzed for tin. If the sample contains over 2 per cent. of tin, another addition of the flux mixture is used; when this is absorbed, if below 2 per cent. tin, the furnace is ready to be tapped.

The slag is tapped into a cast-iron pot and allowed to overflow and granulate into a large pit, from which it is loaded by a locomotive crane, weighed, sampled, and discarded. The analysis of a representative sample of this waste slag is as follows: SiO<sub>2</sub> 35 per cent., Fe 18 per cent., CaO 23 per cent., Sn 2 per cent. or less.

These furnaces produce tin and alloy. The former is cast into anodes and the latter sent to the blast furnace and used currently on the charge. The metals are tapped separately from the slag, usually after every fourth or fifth charge.

The time of treatment and amount of flux mixture used depend entirely on the percentage of tin in the slag charged. Each furnace completes a charge cycle in 24 hr. and requires to complete the reduction approximately 100 lb. of lime rock and 200 lb. of fine anthracite per ton of slag. The average of the slag charged is 6 per cent. of tin with a limit of 10 per cent. The gases from this operation are not filtered on account of the small amount of tin fume given off in treating low-grade slags. With more than 10 per cent. of tin in the slag charged, it has been found more economical to resmelt the slag in reverberatories that are connected with the baghouse. The alloy produced is utilized in the blast furnace, where it is decomposed.

#### PARTIAL, OR SELECTIVE, REDUCTION PROCESS

Numerous experiments were made to develop a method for producing high-purity tin direct from the ores by an all-fire method. It was found that, by partial reduction of the ore, allowing the greater portion of the tin to enter the slag, the tin contained in the slag would be relatively pure and the metal produced by resmelting the slag would be comparatively free from lead, copper, arsenic, antimony, and bismuth and suitable for all purposes for which tin is used. The metal obtained by the first reduction would be relatively impure, but could be subjected to electrolysis for the recovery of tin.

Previous to 1917, nearly all the Bolivian concentrates received would produce a metal of merchantable quality containing 99 per cent. of tin, or better, when smelted by complete reduction and the product could be sold as common or smelter tin. However, after this date, the concentrates arriving were very much lower grade as to purity and the metal produced by direct smelting was not of merchantable quality. Bismuth, copper, and lead became the predominating reducible impurities. Bismuth has a very deleterious effect on tin for most uses, consequently a modification of the process had to be made and the partial-reduction process was adopted.

The average analysis of 1915-16 deliveries compared to 1917-18 were:

	Pb, %	Cu, %	SiO <sub>2</sub> , %	Fe, %	CaO, %	Zn, %	S, %
1915-16.....	0.045	0.042	2.81	3.25	0.88	None	2.13
1917-18.....	0.16	0.16	2.23	5.4	0.91	None	2.40
	As, %	Sb, %	Bi, %	Sn, %	WO <sub>3</sub> , %	Al <sub>2</sub> O <sub>3</sub> , %	
1915-16.....	0.05	0.20	0.22	70.2	0.3	0.75	
1917-18.....	0.036	0.069	0.80	68.0	0.06	0.95	

With concentrates, listed as 1915-16 deliveries, containing 70.2 part of tin to 0.557 of reducible impurities direct smelting to complete reduction would produce a metal of over 99 per cent. of tin; whereas, with the 1917-18 deliveries, containing 68 parts of tin to 1.225 parts of

reducible impurities, complete reduction would not produce a metal of over 98.2 per cent. tin.

The European smelters, when treating impure concentrates, can dilute these impurities to a point where the metal passes into the trade as standard tin (99 per cent. grade), for which there is a large demand, by using sufficient Straits, Nigerian, Australian, or Dutch East Indies concentrates. This condition does not obtain in the United States, as there is only a small demand for standard tin; moreover, there is no available supply of tin concentrates with which to dilute the impurities.

This process is based on the properties of stannous silicate. The higher oxide of tin ( $\text{SnO}_2$ ) is infusible and does not combine with silica but must be reduced to the lower form first.

In this operation, the more easily reducible impurities, such as lead, copper, arsenic, antimony, and bismuth, are completely reduced, together with some tin, while the balance of the tin is reduced from  $\text{SnO}_2$  to  $\text{SnO}$ , which unites with the silica in the charge to form slag. The slag is essentially stannous silicate practically free from impurities such as lead, copper, arsenic, antimony, and bismuth.

The partial reduction process serves to produce a greater part of the tin contained in the ore as pure tin, leaving the balance relatively impure, which must be treated electrolytically. The process is conducted in two stages.

*First Stage.*—Partial reduction smelting of the concentrates producing an impure metal to be electrolytically refined and a slag high in tin.

*Second Stage.*—Smelting of the slag for the production of pure tin.

Both of the operations can be conducted equally well in the blast furnace or the reverberatories.

### *First-stage Smelting*

The only difference in this smelting from the regular method is the amount of fuel and the fluxes used. Only a small amount of fuel is used for reduction and silica is the only flux. It is important that no lime is contained in the charge. The percentage of coke is regulated to give a hot fluid slag high in tin. The slag fall is governed by the amount of silica present, also the slag fall governs the amount and quality of metal produced and is regulated accordingly. The smelting of this charge is very rapid. The slag is granulated and held for retreatment. The impure metal is cast into anodes.

As much as 70 per cent. of the tin contents of the ore can be caused to enter the slag by the first reduction; the balance is reduced to metal, together with the impurities lead, copper, arsenic, antimony, and bismuth. The quality of the metal so produced is governed by the degree of reduction and amount of slag formed; generally about half of the tin is reduced

so that the resultant metal will not be too impure for electrolysis, also to prevent too large an amount of slag to be resmelted as the metal losses are governed to a large extent by the tin contained in the finished slag. Ordinarily, about 0.75 ton of slag per ton of concentrates is produced of the following analysis:  $\text{SiO}_2$  20 to 25 per cent., Fe 5 to 10 per cent., CaO none, Sn 50 to 60 per cent., which is exceedingly thin and well flowing.

The impure metal produced will assay over 90 per cent. tin, when the original ore contained 68 parts of tin to 2 parts of reducible impurities on a 50 per cent. reduction basis and can, therefore, be easily refined by electrolysis.

This process can be applied equally as well to more impure ores. Bolivian concentrates containing 10 parts of reducible impurities to 50 parts of tin have been successfully treated.

### *Second-stage Smelting*

The granulated slag, high in tin, is resmelted either in reverberatory or blast furnace and the operation is conducted in a similar manner to the slag smelting already described. The tin from this operation is of excellent purity, except as to iron; it is cast into bars for liquation in order to separate it from a dross containing the iron. The slag produced is low in tin and is disposed of to the slag-settling furnaces. Frequently, this slag is lower in iron than the arbitrary saturation point and may be mixed with higher iron slags to get the maximum elimination of iron from the process.

The tin bars, when liquated, produce a metal containing about 99.8 per cent. of tin, or better, which is equivalent in merchantable quality to Straits or Banka tin. No attempt was made to put this on the market as a substitute for Straits, Banka, or Electrolyte tin but it was used for blending in the making of common tin. As the demand for common tin in the United States is limited, the tin refinery was enlarged to handle the entire smelter production and only Electrolytic tin was eventually produced.

### BLAST FURNACE VS. REVERBERATORY

It is not within the scope of this paper to discuss the relative costs of the various processes, but the question has been asked so frequently "which is the better process, the shaft furnace or reverberatory," that it will not be amiss to state that the blast furnace has proved the cheaper. As tin smelting is really a small high-grade operation, the reverberatory furnace is preferably for small tonnages, say 700 or 800 tons per month; but when larger tonnages are available, the blast furnace is preferred. The metal loss and the amount of intermediary or byproducts made is about the same in both cases, slightly less in the blast furnace method.

The question of the comparative amounts of fume produced by each process has often been the subject of discussion. One's first thought would be that the blast furnace should produce the most fume, but, in practice, the volatilized tin is condensed in the cooler regions of the upper part of the shaft and consequently less escapes and goes to the baghouse than in reverberatory smelting.

When tin sulfide is formed in the reverberatores, it is readily volatilized and caught in the baghouse; but when formed in the shaft furnace, the greater part does not escape as fume but is eventually found in the tin pot as a well-defined layer on top of the tin.

The practice at many far eastern smelters is to make the first reduction in numerous small open-top blast furnaces followed by a final reduction of the slag in reverberatory furnaces. In a private communication, it was stated that the metal losses caused by dusting and volatilization at one of these smelters did not exceed 1 per cent. of the total tin contents.

### *Fuel Consumption*

#### Reverberatory smelting.

##### Ore smelting

Reducing coal..... 20 to 30 per cent. per ton of ore

Powdered coal..... 600 to 800 lb. per ton of ore.

##### Slag smelting

Reducing coal..... 10 to 20 per cent. per ton of slag

Powdered coal..... 800 to 900 lb. per ton of slag.

##### Blast furnace smelting

Coke..... 14 to 18 per cent. per ton of charge.

### ELECTROLYTIC REFINING

Tin is in a most desirable position in the electromotive series of the metals for electrolytic refining. The only impurity of frequent occurrence that stands equal or close to tin and would dissolve is lead, all the others being below tin.

The potential series of the metals, as given by Ostwald, is according to the following law: "It is possible to arrange all the metals in a single series in such a way that each precipitates all the metals following from their aqueous solutions, but is precipitated by each of the preceding ones." In accordance with this law a partial list is as follows:

- |            |           |             |             |
|------------|-----------|-------------|-------------|
| 1. Zinc    | 4. Cobalt | 7. Lead     | 10. Arsenic |
| 2. Cadmium | 5. Nickel | 8. Antimony | 11. Copper  |
| 3. Iron    | 6. Tin    | 9. Bismuth  |             |

Practically, lead is the only impurity that dissolves; consequently the electrolyte must contain a radical that will form an insoluble compound

with lead, such as a sulfate, chromate, fluoride, etc. The other metals occurring as impurities in tin (arsenic, antimony, bismuth, copper, etc.) are not dissolved and remain in the anode slimes.

The requirements that a tin electrolyte should possess are: (1) It must readily dissolve tin from the anode and thus prevent the anode from becoming passive or insoluble, with consequent high voltage and polarization; (2) it must be a good conductor of electricity; (3) the cathode deposit must be adherent.

Tin is a very crystalline metal and the cathode deposit from most electrolytes consists of long dendritic, or needle-like, crystals. These crystals are loosely attached and grow rapidly, touching the anode causing short circuits. The tin deposits for satisfactory work should be smooth, dense, and adherent. To obtain such a deposit from most tin electrolytes, an addition agent is necessary. The electrolysis of tin had not been considered commercially practical by many metallurgists on account of these difficulties and the venture was undertaken with considerable apprehension.

In the early part of 1915, the late Robert L. Whitehead was detailed to investigate various electrolytes for tin refining, such as hydrochloric acid, sulfuric acid, hydrofluosilicic acid, hydrofluoboric, sodium stannate, sodium sulfo stannate, etc. After extensive experiments, hydrofluosilicic acid was selected as being the most satisfactory electrolyte.

The electrolytes and addition agents that have been used are protected by a series of patents:<sup>3</sup>

#### *Description of Electrolytes*

The hydrofluosilicic acid bath was used from April, 1915, to October, 1917, and consisted essentially of  $\text{H}_2\text{SiF}_6$  with sufficient  $\text{H}_2\text{SO}_4$  to prevent lead from depositing by precipitating it as lead sulfate. The approximate analysis of the electrolyte was:

Specific gravity.....	1.20
Hydrofluosilicic acid.....	20.0 per cent.
Sulfuric acid.....	0.1 per cent.
Stannous tin.....	6.0 per cent.
Total acid in terms of $\text{H}_2\text{SiF}_6$ .....	20.15 per cent.
Addition agent.....	glue

The deposit was only fair, not being dense, but sufficiently adherent to run 48-hr. cathodes. The anode corrosion caused considerable trouble frequently occasioning high voltage with deposition of  $\text{SiO}_2$  at the anode.

<sup>3</sup> R. L. Whitehead: Electrolytic Refining of Tin. U. S. Pat. 1157830 (1915).  
 H. H. Alexander: Electrolytic Refining of Tin. U. S. Pat. Ser. 434124 (1920).  
 C. P. Linville: Electrolytic Tin. U. S. Pat. Ser. 434118 (1920).  
 J. R. Stack: Electrolytic Process. U. S. Pat. Ser. 434114 (1920).  
 J. R. Stack: Process of Recovering Tin. U. S. Pat. Ser. 526871 (1920).  
 F. C. Mathers: Electrolytic Refining of Tin. U. S. Pat. 1397222 (1921).



*Glue-cresylic Acid Addition Agent*

One of the salient features of the process is this addition agent, which was introduced in August, 1917. It was first used successfully in the tin-fluosilicate bath and later adopted in all other electrolytes used. The addition agent commonly used is crude cresylic acid, added in the form of an emulsion with the glue. Many other coal-tar products analogous to cresylic acid can be used as well. The use of these reagents is distinctly novel and credit for the invention is due to Prof. F. C. Mathers of the University of Indiana.

The action of this addition agent produces a dense, smooth, adherent deposit of tin free from growths and frequently shows the vertical striations familiar in copper deposits. Many theories have been advanced as to the action of addition agents, such as: (1) They act as a restraining agent to prevent the formation of a crystalline deposit. (2) They migrate by the action of the current and form a film or envelope around the cathode, thus insuring even distribution of the current and preventing the formation of points of high current density. (3) They form a compound with the metal from which the metal deposits (simultaneously with the metal from other compounds) in a smooth non-crystalline form or in compact blunt crystals. When this form of crystallization has once been established, the metal subsequently deposited tends to follow the same form. (4) The addition agent actually deposits at the cathode together with the metal causing it to deposit in a non-crystalline form of fine blunt crystals.

The theory that the addition agent deposits with tin has been found to be a fact in some instances. In all tin electrolytes used, the addition agent becomes depleted at a constant given rate, varying from  $\frac{1}{3}$  to 3 lb. of glue and 8 to 16 lb. of cresylic acid per ton of tin refined, depending on the character of the electrolyte used. Small fractions of 1 per cent. of hydrochloric acid retard the action of the addition agent.

*Sulfuric-hydrofluosilicic Electrolyte*

This bath was used from October, 1917, to April, 1920, and consisted essentially of sulfuric acid with sufficient hydrofluosilicic acid to prevent the formation of basic salts of tin. The approximate analysis of the electrolyte is:

Specific gravity.....	1.15
Sulfuric acid.....	8.0 per cent.
Hydrofluosilicic acid.....	5.0 per cent.
Stannous tin.....	3.0 per cent.
Total acid in terms of $H_2SO_4$ .....	11.4 per cent.
Addition agent.....	glue and cresylic acid emulsion.

The bath offered many advantages over the straight fluosilicate electrolyte. The mastic-lined tanks, hard-rubber solution lines, bronze

pumps, etc. were replaced with lead. Better anode solubility was obtained without decomposition of  $\text{H}_2\text{SiF}_6$  during electrolysis.

### *Sulfuric-sulfonic acid Electrolyte*

This bath has been used from April, 1920, to date; that is a sulfonic acid was substituted for hydrofluosilicic acid to prevent the formation of basic salts of tin, which occur when  $\text{H}_2\text{SO}_4$  is used alone and render the anode insoluble.

The sulfonic acids can be made from benzol, phenol, cresol, toluene, naphthalene, and other aromatic hydrocarbons, by mixing with strong sulfuric acid and heating according to conventional methods for the manufacture of sulfonic acids. If made, for example, from phenol, the new compound, called phenol sulfonic acid, is produced. This is an avid solvent for tin and other metals forming a soluble salt with lead in contradistinction to  $\text{H}_2\text{SO}_4$ .

If an electrolyte is made up containing 10 to 15 per cent. of either cresol or phenol sulfonic acid, 0.5 to 1 per cent. of  $\text{H}_2\text{SO}_4$  to prevent the deposition of lead, and 2 to 4 per cent. of stannous tin, an excellent cathode deposit of tin can be obtained without the use of an addition agent.

The present bath consists essentially of sulfuric acid with sufficient aromatic sulfonic acids to prevent the formation of basic salts of tin. The approximate analysis of the electrolyte is:

Specific gravity.....	1.12
Sulfuric acid.....	8.0 per cent.
Cresol-phenol sulfonic acid.....	4.0 per cent.
Stannous tin.....	3.0 per cent.
Total acid in terms of $\text{H}_2\text{SO}_4$ .....	10.2 per cent.

The usual addition agent, consisting of glue and cresylic acid emulsion, is added daily in sufficient quantity to produce a dense, smooth, adherent deposit of tin. This electrolyte fulfills all the requirements for a satisfactory tin bath in regard to good cathode deposit, conductivity, soft anode slimes, and uniform anode corrosion. The weak liquors, or wash waters containing electrolyte from washing cathodes and slimes, can be evaporated without decomposition.

### REFINING OPERATIONS

The refinery is similar in arrangement to the usual multiple-tank room. The tanks, 340 in number, are constructed of wood; the inside dimensions are 131 by 41 by 42 in. deep; they are lead lined and properly insulated and are served with overhead cranes.

Electrically driven centrifugal pumps of the vertical type are used for circulation of the electrolyte. The rate of flow through each tank is

about 5 gal. per min. The overflow from the tanks returns, by gravity, to the heating tanks where the solution is maintained at a temperature of 95° F. The circulating pumps are connected to these heating tanks and the electrolyte is kept in continuous circulation throughout the system.

The current is supplied by a steam-driven generator. A current load of 3600 to 4500 amp. is carried, which corresponds to a current density of 8 to 10 amp. per sq. ft. of cathode surface. Under normal working conditions, the voltage required per cell is from 0.3 to 0.35 volts measured across the tank. The current efficiency is about 85 per cent., assuming 1 amp.-day deposits 0.117 lb. from a stannous solution.

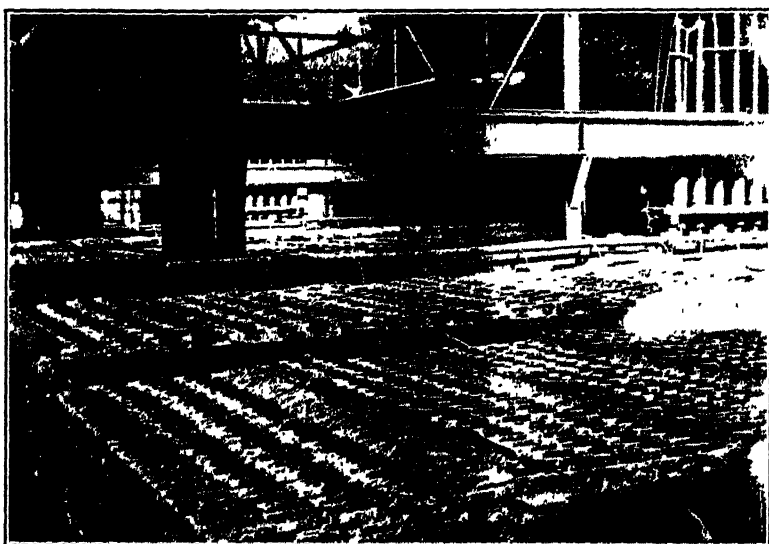


FIG. 4.—TIN REFINERY.

The anode tin from the smelter contains from 90 to 99 per cent. of tin and varying amounts of impurities. A representative sample is: Lead 1.0 per cent., copper 0.25 per cent., arsenic 0.15 per cent., antimony 0.25 per cent., bismuth 1.0 per cent., tin 96.0 per cent. The anodes are cast with the usual extension lugs and the submerged part is 33 by 36 in. wide; they are about  $1\frac{1}{4}$  in. thick and weigh about 350 pounds.

The cathode starting sheets are 34 by 37 in. wide and weigh between 8 and 10 lb. each. These sheets are made by pouring molten electrolytic tin over an inclined steel table of the size and shape of sheet desired, a method similar to that used for making starting sheets for the electrolytic refining of lead.

Each tank contains 26 anodes and 27 cathodes, which are placed alternately and equidistant, the anode spacing being  $4\frac{1}{2}$  in. between centers.

After 7 days of electrolysis, the cathodes weigh about 100 lb. and are removed from the tanks, carefully washed, and melted in a 50-ton capacity cast-iron kettle; then cast into bars of marketable form, weighing 100 lb. and stenciled Electrolytic Tin. New sheets are placed in the tanks and electrolysis again started. Three cathodes are obtained from each anode. After about 75 per cent., by weight, of the anodes has been dissolved, they become too thin to conduct the current efficiently and are removed as scrap, remelted, and cast again into anodes. Each day, the requisite number of tanks of scrap are pulled and replaced with



FIG. 5.—ELECTROLYTIC TIN.

new anodes, so that at the end of 21 days, which is the life of the anode, the circuit of tanks has been completed.

As tin stands above copper, arsenic, antimony, and bismuth in the galvanic series of the metals, none of these will dissolve from the anode, in the presence of the large excess of tin; they therefore remain in the anode slimes. Also, the precious metals will go into the slimes. The usual reagent for precipitating the lead to prevent its deposition at the cathode is  $\text{H}_2\text{SO}_4$ . It has been determined that about half of the lead contained in the anode slimes is present as  $\text{PbSO}_4$  and the balance as a complex alloy.

The tin-anode slimes adhere to and closely maintain the form of the anode, so before the scrap anodes are removed the slimes are carefully

scraped off, filter pressed, washed, and sent to a department for treatment and recovery of the values. Approximately 5 per cent. of slimes is produced per ton of tin refined, containing about 30 lb. of tin per ton of metal refined; or 98.5 per cent. of the tin is deposited from the anodes.

A representative analysis of the anode slimes is: Lead 20 per cent., copper 5 per cent., arsenic 3 per cent., antimony, 5 per cent., tin 30 per cent., bismuth 20 per cent.

Following is a comparative analysis of electrolytic and other brands of tin. The samples were taken at users' plants and the analyses were made by the Perth Amboy laboratory:

	Pb, %	Cu, %	As, %	Sb, %	Bi, %	Sn, %	TOTAL, %
May, 1917, Electrolytic.....	0.07	0.015	0.004	0.002	0.007	99.88	99.978
Penang.....	0.023	0.045	0.01	0.019	0.009	99.88	99.986
April, 1918, Electrolytic.....	0.007	0.03	0.006	0.012	0.015	99.93	100.000
Penang.....	0.03	0.055	0.04	0.04	0.015	99.80	99.980
May, 1919, Electrolytic.....	0.002	0.010	0.005	0.005	0.017	99.93	99.969
Banka.....	0.005	0.015	0.067	0.033	0.01	99.84	99.970
Straits.....	0.01	0.010	0.018	0.024	0.02	99.89	99.972
June, 1920, Electrolytic.....	0.03	0.025	0.005	0.005	0.03	99.90	99.985
Straits.....	0.16	0.05	0.02	0.02	0.011	99.72	99.981
Dec., 1921, Electrolytic.....	0.0025	0.02	0.003	0.004	0.015	99.94	99.985
Straits.....	0.055	0.07	0.03	0.03	0.029	99.77	99.984

This tabulation shows that the Electrolytic tin is lower in the impurities lead, copper, arsenic, and antimony and higher in tin than the foreign high-grade brands of tin.

Electrolytic tin cannot be surpassed for uses that necessitate high-purity tin. Although for some uses, such as tin plating, on account of its high purity it is necessary to add small percentages of impurities in order to produce the same effect as obtained with Straits or Banka tin. It has been demonstrated that when the metal was too pure the desired thickness of coating would not be as readily produced as when limited amounts of impurities were present. It is natural to suppose that certain ingredients would be more desirable than others, hence the high purity of electrolytic tin permits adjusting the composition of the metal to that found best for any particular use.

#### TIN LOSSES

The amount of slag produced in smelting Bolivian concentrates is determined by the iron contents. When treating concentrates containing 8 to 10 per cent. iron, the tin loss in slag alone is 1.5 to 2 per cent. With higher iron contents, this loss increases proportionately. Other sources of loss are in handling, dusting, and fume. The usual loss in electrolyte refining is 10 lb. per ton of tin refined on 97 per cent. tin anodes and proportionately greater on lower grade anodes.

By producing electrolytic tin containing 99.9 per cent. tin instead of standard tin containing only 99 per cent. tin the apparent loss is greater. Even though electrolytic tin is a superior metal, sight must not be lost of the fact that in smelting these impure ores and disposing of the product as 99 per cent. or standard tin, 1 per cent. of impurities are disposed of as tin; when in the electrolytic process, there is an additional loss of at least 10 lb. per ton of electrolytic tin produced which, if added to the 1 per cent. of impurities sold, makes the apparent loss in the electrolytic process 1.5 per cent. higher than in the European method of treating this ore.

### PRODUCTION OF TIN

The world's production of tin in 1922 was close to 130,000 tons. About 27 per cent. was attributed to the Federated Malay States and nearly 25 per cent. to Bolivia. The latter source, almost geographically antipodal to the former, is rapidly approaching the lead in production. One mine alone in Bolivia has produced over 12,000 tons per annum, and it is expected that, when the developments now in progress are completed, Bolivia will lead in tin production.

The United States imports in 1922 were 154,201,000 lb. or 55 per cent. of the world's production. By far the largest use of tin in this country is in the tinplate industry. This industry made rapid strides immediately after the passage of the McKinley tariff and now the United States predominates in the world's output.

No official specifications for the quality of tin have been adopted; its sale and use are customarily based on brands. One of the largest users of tin for tinplating suggested the following specifications, allowing the maximum percentages respecting the impurities named:

	PER CENT.		PER CENT.
Lead.....	0.04	Arsenic.....	0.05
Copper.....	0.02	Antimony.....	0.02
Iron.....	0.05	Zinc.....	0.05

It can be seen that a pure tin is required for the major use and the following brands are commonly used; *i. e.*, Straits, Banka, and Electrolytic, while Billiton, Singapore, Mt. Bischoff, and Pyrmont can also be used.

The second largest requirement for tin is its use for solder making. As lead is not an objectional impurity, many brands of common tin can be used; some secondary metal is used for this purpose. Pure tin is usually required in making babbitt, britannia metal, tinfoil, and collapsible tubes.

## PRESENT STATUS OF TIN REDUCTION AND REFINING INDUSTRY IN AMERICA

Prior to 1915, tin smelting was negligible in this country. As over 50 per cent. of the world's tin was consumed in the United States, it seemed logical to believe that the industry could be firmly established in America. Concentrates from Bolivia via the Panama Canal to the United States take a favorable rate, also transportation charges on the metal from London to New York are saved. But at present all of the tin smelters in America are closed.

In 1915, the treatment charge on Bolivian concentrates varied from £14 to £18 per long ton, depending on the grade, impurities contained, and so forth. At present, foreign smelters are offering to treat these concentrates for as low as £10 per ton and in some cases even less. Since 1915, labor, fuel, supplies, etc. have advanced in this country approximately 125 per cent.

The situation is briefly explained by an item that appeared in the *New York Sun and Globe* when the National Lead Co.'s plant at Jamaica Bay was closed, which is quoted as follows:

"President Cornish informed stockholders that the company's tin-smelting plant would be closed in the near future, this being necessitated by certain economic changes . . . the National Lead Co. is enabled to secure its needs in England at much lower cost than by producing it in this country."

The future of tin smelting in America is uncertain. Will ore-dressing methods improve to the point where the concentrates will produce, on smelting, a metal comparable to Straits or Banka with correspondingly small metal losses, or will the present milling practice continue? If the latter should be the case, the Perth Amboy methods and electrolytic refining, as here outlined, solves the problem of producing pure tin from Bolivian concentrates.

## DISCUSSION

EDWARD F. KERN,\* New York, N. Y.—Has there been any work done on the variation of the slag and silica with the object of reducing the tin content of the slag?

J. R. STACK.—Siliceous slags containing 35 to 40 per cent. silica have given us the best results in tin smelting. In many instances, 30 to 32 per cent. silica slags have been run, but with slags containing over 35 per cent. silica the tin contents are invariably lower. This is particularly evident in the blast-furnace smelting. Of course, the more silica used the greater will be the amount of slag produced. With the average concentrate, we usually produce about 0.5 ton of slag per ton of concentrate.

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\* Professor of Metallurgy, Columbia University.

A well-known electric-furnace company states that finished slags containing only 0.2 to 0.3 per cent. tin can be produced in one operation by electric-furnace smelting without the formation of iron-tin alloy. In this case, the composition of the slag must contain not less than 66 per cent.  $\text{SiO}_2 + \text{Al}_2\text{O}_3$ , that is tin can be selectively reduced from iron at sufficiently high temperature, stated to be about  $1450^\circ \text{C}$ . We have not verified these reactions.

EDWARD F. KERN.—The basis of your calculations is the amount of silica in the ore?

J. R. STACK.—We flux the ore according to the percentage of iron.

EDWARD F. KERN.—And with no iron addition?

J. R. STACK.—Iron is excluded because it increases the amount of slag produced and slag is the medium for the elimination of iron. All iron entering the smelter, in the form of ore is eliminated in waste slag and every ton of waste slag contains tin, usually  $1\frac{1}{2}$  to 2 per cent. We are limited as to the amount of iron that the waste slag can contain, usually 15 to 18 per cent. iron, and consequently iron is not used for fluxing in order to avoid increasing the amount of slag produced.

EDWARD F. KERN.—At the Mattawan plant of the American Tin Smelter, William Allen Smith made a number of smeltings, and found the slag running about 28 or 30 per cent. of silica and the ratio of lime to iron oxide throughout practically 1 to 1.5 and the content of hard head practically nil. It seems to me, picking out the slag that had a low formation temperature and low melting point, the tin recovery was very much higher. I have done some work along that line in the laboratory which holds out that same summary of results, pointing to that fact.

J. R. STACK.—From 28 to 38 per cent. silica?

EDWARD F. KERN.—From 28 to 30 per cent. of silica, keeping the iron oxide at 25 to 30 per cent. and the lime at 25 to 18 per cent.

R. L. HALLETT, Brooklyn, N. Y.—I know little about the operations at Perth Amboy, but I was connected with the operation of the Brooklyn plant of the Williams Harvey Corp'n. It was the necessities of the war, more than anything else, that prompted us to enter this field; the Perth Amboy smelter was started some time prior to ours. Economically, there seemed to be no reason why Bolivian ores should not be smelted in the United States, as well as any other part of the world, particularly as the United States consumes such a large part of the world's production of tin. If the ores were smelted in Bolivia, the tin would be exported to the United States. By smelting the ores in the United States, the proposition would be almost as good economically because the freight on the concen-



trates is not much higher than the freight on the tin would be, considering that the tin bullion would have so much greater value.

The industry was started and at the Williams Harvey plant, technically, it was very satisfactory. The smelting plants in this country did just as good metallurgical work as any others, probably better, and for a while tin smelting looked like a permanent industry; but, not through any superior metallurgical operations, tin smelting in England has reached a point where the work can be done so much cheaper, largely through lower labor costs, that it is unprofitable for this country to compete with England, unprotected as we are by any tariff.

Bolivia is one of the great sources of tin. Its production is now approaching if it has not already passed that of the Straits Settlements. Being such a dominant factor in the tin supply of the world, we must look to the Bolivian ores as one of the great sources. These ores are just as available to the English smelters as to the American.

C. R. HAYWARD,\* Cambridge, Mass.—It was suggested to me that the reduction of tin ore, in order to get away from slag losses and the difficulties with slag in smelting, should begin with the treatment of the concentrates. Unfortunately, a long series of experiments is necessary to establish a commercial process for cleaning the concentrates. Some laboratory experiments, however, showed that once you clean the concentrates and produce what is practically pure oxide you can easily reduce with gas. Unfortunately when impurities are present, the reduced tin will not agglomerate readily; after the concentrates are cleaned the tin will agglomerate readily in metallic form. My recollection is that the reduction of the oxide takes place completely somewhere between 800° and 900° C. and very quickly.

When reducing the tin oxide, if it is kept under reducing conditions, there apparently is very little volatilization of the tin; when there is a slightly oxidizing condition, fumes of tin appear. In some experiments, in a small laboratory blast furnace, I found high volatilization of tin.\* When discussing this with a man who traveled recently in Germany, I was told that some one in that country has worked out a process for complete volatilization of the tin in a blast furnace, recovering it as oxide, thus purifying the ore; then, the pure tin oxide is readily reduced by gas. If we are to treat tin ore in this country, it must be by some new method. We can, by cutting down labor costs, compete with England.

EDWARD F. KERN.—This matter of gaseous reduction of tin ore will be the revolutionizing of the tin-smelting industry. In 1911, Mr. Fan Chen, a Chinese student, was very much interested in tin reduction, so we started out to determine the temperature at which tin oxide is reduced, and found the reduction temperature of the oxide, using mixtures of

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\* Associate Professor of Metallurgy, Massachusetts Institute of Technology.

ordinary New York City illuminating gas. Last year, a graduate ran through the reductions of tin concentrates using gas similar to producer gas. It was found, by means of carbon monoxide, that the reduction was not complete, but when mixtures similar to enriched producer gas were used the reduction of tin was complete. That could be carried out at approximately 800° C., and the residue left was practically a dry reducer, with a reduction of 90 to 95 per cent. of the tin, without the production of any slag.

Just this past term, another student has taken up the temperature of reduction of tin oxide by the use of charcoal, coke, anthracite, and bituminous coal, and has determined the temperatures of reduction quite accurately with that same idea in mind; not holding entirely to gaseous reduction but using solids, whatever may be available at the mines or wherever the work is to be done. Anthracite was found to be the most suitable of these reducing agents at temperatures between 800° and 850° C. It being heavy, the reduction was practically complete, and by using a furnace that enabled the ready stirring of the mixture, and allowing the tin which is molten at 230° C. to liquate from the other product which is a dry residue, and without the reduction of any iron. It will do away with the "hard head" entirely, and get merely the reduction of the tin oxide, and the lead that might be present.

With regard to the iron content of the ore, the temperature can be so readily controlled that only the tin is reduced. I think the metallurgy of tin will change to the dry reduction. In the reduction of tin oxide, considerable experimental work has been done by means of hydrogen, and circulating the unconsumed hydrogen back to the reducing chamber.

J. R. STACK.—Several years ago, we investigated the gaseous reduction of tin ores. Although it had several possibilities, we concluded it could not economically compete, at Perth Amboy, with the blast-furnace smelting. After the tin has been reduced, there remains the problem of separating from it the residue, which consists of iron and the slag-forming constituents. This residue occludes tin and may require additional treatment, either smelting or leaching. On reviewing the literature, we found that this method, under the name of Chenwill process, had been established on a small commercial scale in England about 1910. Tin was said to have been reduced from the concentrates by treatment with a reducing gas; evidently the venture was not a commercial success.

EDWARD F. KERN.—I doubt whether that would call for another smelting or leaching, because, in starting with the tin concentrates, you will have 65 to 72 per cent. of tin; which means 85 to 95 per cent. of  $\text{SnO}_2$ . If the concentrates contain 10 per cent. of gangue materials, that means the slag produced by smelting will not weigh less than half of the tin

concentrate. Say for a 72 per cent. tin concentrate you would have half the weight in resulting slag or 36 parts slag per 100 parts concentrates. The gaseous reduction will give you a dry residue low in tin. Should you have chlorides present, the addition of lime overcomes that, makes a very dry residue, and prevents sticking. I still maintain that the gaseous reduction is the coming process for reducing tin concentrates.

R. L. HALLETT.—At the Williams Harvey plant we used, very successfully, a regular fire-smelting process, approximately the same as has been used in England for many years, not making as pure a grade of tin as is made by the electrolytic method, but making tin suitable for many purposes.

The fire-smelting process has gone through many years of development. While it is sometimes said that little progress has been made in tin smelting, slowly year after year, improvements, mechanical and otherwise, have been added until tin smelting today, even by the old fire process, is much different from what it was some years ago.

As to gaseous reduction, it would depend on the amount of tin left in the residue whether a method of that kind would pay. It is a simple matter to reduce tin from tin concentrates. The temperature of reduction is low. The mixture can be easily fluxed. It requires only a small amount of flux and that part of the process is not at all difficult. The metallurgical differences are not great, after the process has been thoroughly studied and the details worked out. Reduction with gas, if it left a residue that you could afford to throw away, which is still problematical, might take care of the first stage, but there would still be the reduced impurities that must be taken care of. There would be an expensive preparation of the ore to begin with, so that the actual reduction in the smelting furnace, the first stage furnace, is only one of the problems that we encounter in the first smelting of tin.

WILLIAM H. BASSETT, Waterbury, Conn.—During the war, we used a little electrolytic tin. Our general problem is twofold. One is the use of tin in making tinned sheet copper, where we must keep away from such impurities as iron; in this, a good deal of residue is made through the solution of the copper itself, the melting point of tin increasing on account of alloying and crystals of the copper-tin alloy separating out. The other is the use of tin in alloys for making bronze springs that, among other things, are used for delicate electrical apparatus. Here very pure tin must be used because impurities, such as lead, bismuth, and antimony, make the springs brittle. It does not make any difference to us whether the tin is electrolytic or fire refined; but for alloys it must be pure, and for tinning it must be free from those elements forming crystals that separate out from the tin bath at relatively low temperatures.

R. C. CANBY, Wallingford, Conn.—I am one of the few people who produced American tin. It was not so very much that we produced in El Paso, but it was quite pure tin. We had none of the difficulties that we hear were encountered in treating these Bolivian ores. Our ore was granite with cassiterite. We got very pure cassiterite concentrate and melted that down in an oil-fired furnace. Perhaps the most important problem now is the improvement in the concentrating of the crude Bolivian ore.

H. G. S. ANDERSON, New York, N. Y.—I am not a tin metallurgist, but I have had some experience in the reduction of tin without slagging. We used a small circular muffle furnace about 3 ft. in diameter. Carborundum tubes led through the upper part of the furnace and under the regular arch. The hearth rotated and the tin concentrate, mixed with sufficient reducing agent in the form of partly distilled coal, was introduced into the furnace, and the operations were continuous.

The furnace was heated by oil, which was burned in the carborundum tubes and the heat conducted through the tube and radiated to the charge, so that no combustion gases mixed with the reduction gases whatever. The temperature was about 950° to 980° C.; it could have been operated at a lower temperature, but the reduction would not have been fast enough for what we might consider economical use. The tin could be seen reducing and formed a circular bath about 6 or 8 in. out from the point at which it was introduced into the furnace. The hearth was iron or steel, about  $\frac{1}{8}$  in. thick and was filled with carbon; in the lower part the carbon was coarse, but it became finer as it neared the charge. The tin sank down through the hearth and was drawn off continuously at the bottom.

Any iron present at that temperature will reduce and form hard head, which forms a skull over the top of the hearth. However, until considerable of that hard head accumulates, the tin that has been reduced and does not alloy with the iron will work its way through this hard head and can be drawn off continuously. The grade of tin, with the concentrate containing originally about 6 or 7 per cent. iron was, without any further refining, about 99.75.

The apparatus was a modification of a process for making sponge iron. At the time we were developing the sponge process, a friend interested in it thought he might be able to apply this modification in apparatus to the reduction of tin. As a result he shipped us 5 tons of Bolivian concentrates and we carried on these experiments producing sixty bars of tin in this manner, which assayed about 99.75 per cent. We used a partly distilled coal. Evidently the tin oxide was reduced by carbon monoxide, because the carbon monoxide in the muffle gases was 85 per cent. monoxide, and 15 per cent. carbon dioxide.

EDWARD F. KERN.—Was there hydrocarbon?

H. G. S. ANDERSON.—Very little hydrocarbon. The coal contained about 10 per cent. volatile, so all the light oils would be extracted from the coal and prevent the light oils distilling the charge. The light oils form a large volume of gas and a suspension of lampblack in the muffle producing an effect like clouds on a cloudy day. There may have been a small amount of hydrocarbon there, but it would have been very small compared to the amount of carbon monoxide.

A small amount of the tin, probably 5 per cent., was carried over by the rabbles into the discharge with the scoria. This came out in a small pellet form, and was later concentrated and melted down as tin. If there was any iron present, it would have affected this tin to the extent that it went over, but most of the iron alloyed with the tin in the furnace and formed the hard head in the furnace. After we cleaned the tin concentrate, as suggested by Professor Hayward, there was little iron present and practically no metals beside the tin. It is the easiest thing in the world to produce tin in this way when the tin concentrate has been cleaned.

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## Hydrometallurgy of Lead\*

By OLIVER C. RALSTON,<sup>†</sup> BERKELEY, CALIF.

(New York Meeting, February, 1924)

A DEFINITE field of usefulness has developed for the brine-leaching processes of removing lead from ores and other products, so this paper reviews the developments, both in practice and in research, that have taken place since the publication of two earlier papers on this subject.<sup>1</sup> Several commercial plants are now in operation and a number of semi-commercial test plants have been operated in an effort to determine the limitations of brine leaching and to compare the results with other forms of treatment.

Briefly, the brine leaching of lead depends on the fact that lead chloride and lead sulfate are soluble in saturated sodium-chloride solutions. In dilute brines, the solubility of the lead salt is less than in pure water; but in the strong brines, the solubility is greater than in pure water due, supposedly, to the formation of a double sodium-lead chloride. This is seen in Fig. 1, which shows the results of M. Demassieux<sup>2</sup> on the solubility of lead chloride in sodium-chloride solutions of different concentrations and at three temperatures. The curves are not those given by Demassieux but are calculated from his results in order to convert them to units common in metallurgical work. The right-hand branch of each curve shows that if the solution is kept in contact with solid sodium chloride the lead chloride can be almost entirely displaced from solution, but that brines which are saturated with sodium chloride, but are not in contact with the solid salt, have a very high solubility for lead chloride. The diagram gives the analysis of the solution in grams of lead per liter, although the substance actually in solution is lead chloride. At 100° C. as much as 100 gm. of lead per liter can be obtained; but at lower tem-

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\* By permission of the Director, Bureau of Mines of the Department of the Interior.

<sup>†</sup> Assistant Chief Metallurgist, Bureau of Mines.

<sup>1</sup> Lyon and Ralston: Innovations in the Metallurgy of Lead. Bureau of Mines Bull. 157 (1918).

Ralston, Williams, Udy, and Holt: Salt in the Metallurgy of Lead. Trans. (1917) 57, 634.

<sup>2</sup> M. Demassieux: *Comptes Rendus* (1914) 158, 702.

peratures less lead is dissolved, until at about 13° C. the maximum solubility of lead chloride allows only about 17 gm. of lead per liter. A high lead ore requires almost one ton of solution for every unit (20 lb. = 1 per cent.) of lead in the ore.

The effect of temperature on the solubility of lead chloride in brines is shown in Fig. 2, which is derived from Fig. 1 and gives the upper and

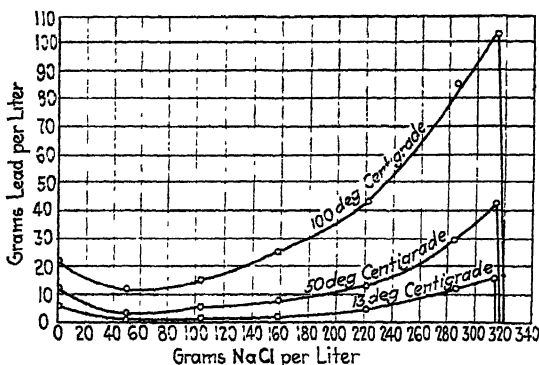


FIG. 1.—SOLUBILITY OF LEAD CHLORIDE IN SODIUM-CHLORIDE SOLUTIONS.

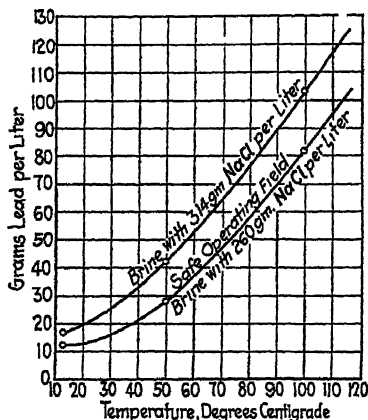


FIG. 2.—EFFECT OF TEMPERATURE ON SOLUBILITY OF LEAD CHLORIDE IN BRINES.

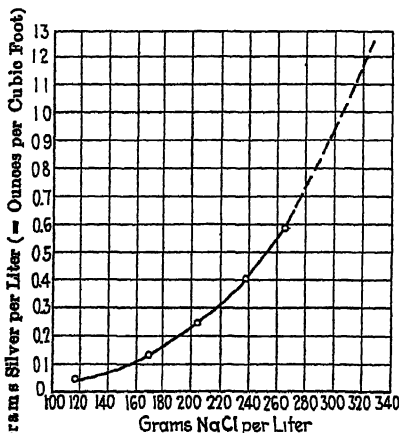


FIG. 3.—SOLUBILITY OF SILVER CHLORIDE IN SODIUM-CHLORIDE BRINES.

lower concentrations of brine that have been found practical; between these two curves is the safe operating field. A weaker brine has not sufficient dissolving power and a stronger brine cannot be prepared except at the expense of throwing lead chloride out from solution.

Although the addition of sulfates to most solutions of lead will form an insoluble precipitate of lead sulfate, this is not true for brines; in fact lead sulfate can be dissolved by the brine, apparently it is altered to lead chloride and the sulfate radical combines with sodium. An

accumulation of sodium sulfate in the solution is not desirable, as it allows less sodium chloride to stay in solution and to that extent dilutes the effective leaching solution; therefore, in most commercial practice, as at present developed, where sulfates are invariably present, solutions with a dissolving power near the lower limit of Fig. 2 are more common than those near the higher limit.

A strong brine also dissolves cuprous chloride and silver chloride, both of which are practically insoluble in water. Quantitative figures are not available for cuprous chloride but the solubility for silver chloride in strong brines has been determined by Forbes<sup>2</sup> and his recalculated data are given in Fig. 3. Extrapolation had to be used to get the solubility at concentrations of salt necessary for efficient extraction of the lead. The solubility is given in grams of silver per liter and also in (approximately) ounces of silver per cubic foot of brine. For the strong brines, about 1 oz. of silver will be extracted by 1 cu. ft. of brine. Proper proportioning of solution to ore in order to extract all of the silver can be made on this basis; for most ores, the ratio necessary to extract all of the lead gives a great margin of safety for the silver.

Whereas the lead can be dissolved in a neutral brine, the silver is so easily precipitated from the solution on such substances as zinc sulfide that almost invariably the brine must also contain small amounts of acid or of ferric chloride or cupric chloride, all of which tend to redissolve any precipitated silver sulfide.

### PRODUCTS REQUIRING TREATMENT

Brine leaching can be used for any product containing lead chloride or lead sulfate and silver chloride or silver sulfate. Acidified brines also tend to attack galena and the sulfide minerals of silver, especially if the solution also contains the higher chlorides of iron or copper. A brief review of the products to which the brines have been adapted is given.

1. *Electrolytic zinc plant tailing.* Most of the lead originally present in the ore is present in this tailing as sulfate; part of the silver and much of the copper also are in a soluble condition. On that account, rather large sums of money have been spent in testing the adaptability of brine leaching to the treatment of zinc-plant tailing at Great Falls, Mont., Trail, B. C., Kennett, Calif., and Hobart, Tasmania. The general details of the experimental work at these various plants are given later.

2. *Lead-sulfate flue dust from lead and zinc smelters.* The application of brine leaching to treatment of this product has been tested at a number of smelters and by several inventors. As is well known, lead smelters cannot normally treat large percentages of lead-sulfate dust and always

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<sup>2</sup> G. S. Forbes: *Jnl. Am. Chem. Soc.* (1911) **33**, 1937.



try to avoid it or at least not to allow the percentage used in the blast-furnace charge to rise above a rather low figure.

3. *Lead-sulfate sludges from sulfuric-acid chambers.* The lead of the chamber walls is gradually sulfated (3 lb. lead per ton acid produced) and it is common practice to clean out and repair the lead chambers every three or four years and ship the lead-sulfate sludge to a lead smelter, if one is within economic distance.

4. *Oxidized ores of lead containing lead carbonate or lead sulfate.* If these ores do not contain too much limestone or other acid consumers, an acidified brine (containing sulfuric acid) can be used for the extraction of lead carbonate whereas a neutral brine will extract the lead sulfate from almost any ore. This is being tested on river accumulations of tailing by the Bunker Hill & Sullivan Mining, Smelting & Concentrating Co. in Idaho and has been investigated by several other companies. Silver ores containing oxidized minerals of lead are given a chloridizing roast at two plants in Utah and the lead is recovered from the ore, together with the silver, by the use of brines.

5. *Concentrating mill tailing containing lead sulfide or silver sulfide, or both.* This type of material is receiving serious attention by the Bunker Hill & Sullivan Co.

6. *Complex zinc-lead-iron sulfide ores.* Numerous methods of chloridizing and brine leaching have been invented and tested. Nearly all of the large companies in the world that produce large amounts of zinc-sulfide concentrate containing lead have investigated various chloride-volatilization processes or brine-leaching processes for the removal of the lead and silver.

#### METHODS OF CONVERTING LEAD TO SOLUBLE FORM

For oxidized ores, as just mentioned, lead sulfate is directly soluble in the brine and lead carbonate is soluble in acidified brine. Oxidized ores also yield to either sulfate or chloride roasting preceding a brine leach. Methods of treatment that also form ferric chloride or other multivalent chlorides in the solution are also applicable to lead carbonate, as the latter reacts with ferric chloride, precipitating basic ferric chloride or ferric hydroxide and giving off carbon dioxide so that the lead goes into solution as lead chloride. Chloridizing roasting with salt in a shaft roaster is practiced at two plants in the Tintic district of Utah, as described elsewhere in this paper.

For sulfide ores, one of the simplest things to do is to give a low temperature roast (400° to 550° C.), under which conditions the galena is sulfated easily and almost completely. This was investigated and reported by the Bureau of Mines in previous papers (*loc. cit.*). A cleverly designed roaster for this purpose is now being developed at the Bunker Hill & Sullivan pilot plant.

Chloridizing roasting of lead-sulfide ores containing silver is another favorite method and patent literature is full of processes that are variations of this idea. It was reported, both by the Bureau of Mines in the publications just referred to and by Larson<sup>4</sup> who worked for several years at Kellogg, Idaho, with a simple lead-silver ore. The use of zinc chloride instead of sodium chloride for heating with complex sulfide ore is advocated by Ganelin<sup>5</sup> and by the Amalgamated Zinc (DeBavay's) Ltd. of Australia,<sup>6</sup> as well as by Harry Hey<sup>7</sup> formerly of the Amalgamated Zinc but later of the Electrolytic Zinc of Australia, Ltd. Heating the ore in an atmosphere containing hydrochloric-acid gas is advocated by the Amalgamated Zinc<sup>8</sup> and by Hey,<sup>9</sup> galena being chloridized before sphalerite. This chloridizing-roasting treatment converts the lead to a soluble form satisfactorily, but one important function of the chloridizing roast is to convert any silver compounds in the lead ore to the chloride form so that the silver chloride may also be extracted with the lead chloride or sulfate by a brine. Heating with ferric or cupric chloride to 150°–250° is advocated by Middleton<sup>10</sup> in order to chloridize the silver. Chloridizing roasting with chlorides of calcium or magnesium at 400°–500° C. is advocated by F. E. Elmore,<sup>11</sup> using moist air to generate hydrochloric acid by interaction with the alkaline-earth chlorides in the charge, which are the actual chloridizing agent. A temperature of over 500° C. cannot be allowed as the zinc sulfide is attacked at higher temperatures, but below it the galena is selectively chloridized. Selective chloridizing roasting with salt is advocated by H. J. E. Hamilton,<sup>12</sup> of Broken Hill, who keeps the roasting temperature below 400° C. in order to chloridize lead and silver selectively without affecting the zinc content of the ore.

Sulfuric-acid treatment of mixed sulfide ore is proposed by several inventors. Elmore<sup>13</sup> uses strong acid (1.84 sp. gr. or 95 per cent.  $\text{H}_2\text{SO}_4$ ) at about 100° C., under which conditions the galena is converted to lead sulfate with liberation of sulfur dioxide and elemental sulfur and the zinc

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<sup>4</sup> C. L. Larson: *Hydrometallurgy of Lead-Silver at the Bunker Hill Smelter Min. & Sc. Pr.* (1917) 115, 275.

<sup>5</sup> Solomon Ganelin: U. S. Patent No. 1396740, 1921.

<sup>6</sup> Brit. Patents No. 135968, 1918; No. 141044, 1920; No. 144280, 1920; No. 151952, 1920. U. S. Patent No. 1402733, 1922.

<sup>7</sup> Harry Hey: U. S. Patents No. 1452858 and No. 1452857, 1922.

<sup>8</sup> Brit. Patent No. 159135, 1921.

<sup>9</sup> Harry Hey: U. S. Patent No. 1384465, 1921.

<sup>10</sup> Percy R. Middleton: U. S. Patent No. 1403516, 1922.

<sup>11</sup> F. E. Elmore: Brit. Patent No. 162026, 1919.

<sup>12</sup> H. J. E. Hamilton: Brit. Patent No. 152289, 1920, and Canad. Patent No. 220917, 1922.

<sup>13</sup> F. E. Elmore: U. S. Patent No. 1441072, 1923; also Brit. Patent No. 127641, 1917, and Canad. Patent No. 217900, 1922.

and other sulfides in the ore are largely unaffected. Christensen<sup>14</sup> has developed a very similar treatment of the ore that produces almost the opposite result. By using acids from 60 to 98 per cent. in strength and heating to their boiling points, the zinc sulfide is attacked and converted to sulfate which is soluble in excess of the concentrated acid. With acids stronger than about 80 per cent., elemental sulfur and sulfur dioxide are evolved and galena is sulfated. With weaker acids, hydrogen sulfide is the main sulfur product and galena is not attacked while the sphalerite is. P. A. Mackay<sup>15</sup> uses fuming sulfuric acid containing considerable dissolved sulfur trioxide to attack the galena and convert it to sulfate.

Strong hydrochloric-acid solution, when heated, will attack galena in preference to sphalerite, according to Elmore,<sup>16</sup> with evolution of hydrogen sulfide. However, the difficulties of heating hydrochloric acid in any commercial material of construction are so great that this method will not be of great interest.

Dilute hydrochloric-acid solution, in the form of a slightly acid saturated sodium-chloride brine, is recommended by Elmore,<sup>17</sup> who adds sulfuric acid to the ordinary brine used in leaching soluble forms of lead; when heated close to the boiling point this solution attacks the galena with evolution of hydrogen sulfide, leaving the zinc sulfide largely untouched. Sulfuric acid is used because it is cheap but means must be taken of preventing deleterious accumulation of sulfates in the brine. Some of the silver in the ore is also dissolved, especially if hydrogen sulfide is removed as fast as formed. The early work by the Bureau of Mines was with acid brines as applied to oxidized ores. Although desultory experimenting was known to the author, Elmore seems to be the first to have published anything on the use of these brines with raw sulfide ore; since then numerous inventors have worked with these brines and the patent literature resulting is too voluminous to review here. Acid brine is of greater importance for the leaching step than for the preparation of the ore for leaching, the subject at hand.

Ferric chloride, usually dissolved in a strong brine of NaCl or of CaCl<sub>2</sub>, has been experimented with by several organizations on a relatively large scale and seems to be well adapted to removing lead and silver from complex sulfide ores. Usually the solution must be heated in order to make it attack the lead and silver minerals vigorously. The

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<sup>14</sup> N. C. Christensen: U. S. Patents No. 1415796, 1917; No. 1434084, No. 1434086, No. 1434088, and No. 1435891, 1922.

<sup>15</sup> P. A. Mackay: Brit. Patent No. 154718, 1919.

<sup>16</sup> F. E. Elmore: Brit. Patent No. 131353, 1918, and U. S. Patent No. 1346642, 1920.

<sup>17</sup> F. E. Elmore: Brit. Patents No. 127641, 1917; No. 181239, 1921; and No. 184628, 1921.

sulfur of the galena is liberated as free sulfur. Perhaps the most work has been done by Hanney,<sup>18</sup> Collins,<sup>19</sup> and Christensen.<sup>20</sup> Hanney worked at the plant of the Consolidated Mining and Smelting Co., of Trail, B. C., which will be described later. Collins is an English inventor and Christensen has been identified with chloridizing roasting and leaching of silver-lead ores in Utah for ten years. Brines containing ferric chloride are more widely used for leaching prepared ore than for attacking raw ore.

### LEACHING SOLUTIONS

A neutral saturated brine of sodium chloride, or a strong brine of calcium chloride or magnesium chloride, will dissolve lead chloride, lead sulfate, and silver chloride so that they may be leached from the ore. Silver is so easily precipitated on other sulfide minerals that its leaching solutions must be acidified or carry some ferric chloride, which redissolves any silver metal or silver sulfide that tends to precipitate; its use is fundamental to the processes of the Amalgamated Zinc (DeBavay's) Ltd., of Australia,<sup>21</sup> of Christensen<sup>22</sup> and of others.<sup>23</sup>

A chloride solution containing excess chlorine is used by Nathansohn<sup>24</sup> in order to take the lead chloride into solution as the more soluble tetrachloride of lead. A leaching solution of brine containing smaller amounts of chlorine is used in the Tainton process (private communication) at the Bunker Hill & Sullivan test plant, Kellogg, Idaho, in order to take lead and silver into solution and prevent reprecipitation.

Ferrous-chloride solution containing 12 per cent. ferrous chloride, which is capable of taking up 3 per cent. of lead chloride at 90° C., is used by DeLuce,<sup>25</sup> who uses ferrous chloride in place of sodium chloride, in spite of the lower dissolving power, to follow an attack of the ore by a 15-per cent. ferric-chloride solution and he thus avoids trouble due to the mixing of the two solutions.

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<sup>18</sup> Wm. H. Hanney: U. S. Patent No. 1456798, 1923; Canad. Patent No. 210188, 1921.

<sup>19</sup> J. J. Collins: Brit. Patent No. 166929, 1920.

<sup>20</sup> N. C. Christensen: U. S. Patents No. 1415796, 1919; Nos. 1434084-5-6-7-8, No. 1455891, 1922; Nos. 1441063-4-5, No. 1456784, 1923.

<sup>21</sup> Brit. Patents No. 135968, 1918; No. 141044, No. 142854, No. 144260, No. 151952, 1920; No. 159135, 1921.

U. S. Patents No. 1384465, 1921; No. 1402732, Nos. 1432858-9, 1922.

<sup>22</sup> *Loc. cit.*

<sup>23</sup> Soc. Anon. Minéraux et Métaux.; Brit. Patent No. 136163, 1919.

Collins, *ibid.*

Solomon Ganelin: *Pat. cit.*

<sup>24</sup> A. Nathansohn: Brit. Patent 187195, 1921; Ger. Patents Nos. 366483-4-5, 1922.

<sup>25</sup> Robert DeLuce: U. S. Patent No. 1251485, 1918.

## PRECIPITATING THE LEAD

The early work of the Bureau of Mines seemed to indicate that electrolytic precipitation in a cell with iron anodes would be economical and satisfactory. This method was tested on a fairly large scale by the Anaconda Copper Mining Co., at Great Falls, Mont., by the Bunker Hill & Sullivan Mining & Concentrating Co., at Kellogg, Idaho, and by the Consolidated Mining & Smelting Co., at Trail, B. C., details of which will be given later.

Since the work with soluble anodes was done, other inventors have been busy developing the electrolysis of brines containing lead in cells with insoluble anodes (graphite) and utilization of the anode products. Flynn and Van Arsdale<sup>26</sup> depolarized the anode with ferrous chloride in the solution; Christensen and others, who use ferric chloride to attack the ore, likewise use insoluble anodes and ferrous chloride in the solution; Tainton<sup>27</sup> generates chlorine at the anode and later uses it in leaching.

Chemical methods of precipitation have also received their due interest and several rather efficient methods have developed. Zinc hydroxide as a precipitate of lead from brines, the precipitate being lead hydroxide, has been proposed by N. C. Christensen and E. H. Snyder, in connection with the possible treatment of complex zinc-lead sulfide ore from Pioche, Nev. This method would allow the removal of the lead and the subsequent recovery of the zinc in brines by precipitation of the zinc as hydroxide, part of which would be returned for precipitating lead. Sodium carbonate, sodium sulfide, and lime are mentioned by Sulman and Pickard,<sup>28</sup> of London, in connection with a proposed modification of the original brine leaching and precipitation processes described by the Bureau of Mines.

In the early chloridizing blast-roasting and brine-leaching mills in Utah, where the recovery of silver and copper was the main object, lead went into solution and part of it was precipitated on the scrap iron used for recovery of the silver and copper, after these two metals had been removed from the solution. This precipitation on scrap iron is very slow at ordinary temperatures but is more rapid if the temperature of the solution is raised. This fact has been utilized in the chloridizing leaching mill of the Tintic-Standard Mining Co., at Harold, Utah. Details of this are given later. The need of using hot brines makes working in the mill uncomfortable and there is some difficulty in cleaning up the precipitated lead.

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<sup>26</sup> F. N. Flynn and G. D. Van Arsdale: *Eng. & Min. Jnl.* (1920) 109, 487; also U. S. Patent No. 1448923, 1923.

<sup>27</sup> U. C. Tainton: private communication.

<sup>28</sup> H. L. Sulman and H. F. K. Pickard: U. S. Patent No. 1265547, 1918.

Sponge iron as a precipitant of lead from brines was probably first experimented with on a relatively large test at Kennett, Calif., in the electrolytic-zinc plant of the U. S. Smelting, Refining and Mining Co., by H. R. Hanley, in connection with the recovery of lead from zinc-plant residue. T. P. Holt has recently operated a commercial plant in the mill of the Tintic Milling Co. at Silver City, Utah, producing sponge iron by a process developed at the Northwest Experiment Station of the Bureau of Mines and using it in recovering lead from leaching solutions. Sponge iron, different from scrap iron, will precipitate the lead as a spongy metal at practically room temperature and does not require heating of the solution to the temperature needed by scrap iron. The precipitation is also rapid and practically complete. As used at Silver City, it is merely placed in beds in long launder-shaped boxes and the solution passed down through it. It can also be pulverized like zinc dust and applied, in the same way that zinc dust is used in cyaniding, for the precipitation of lead, copper, silver, and gold from brine-leaching solutions.

#### USERS OF BRINE LEACHING

The foregoing shows that brine-leaching methods have received wide attention and a number of commercial plants are in operation. In Australia, the Amalgamated Zinc (DeBavay's) Ltd., some of whose inventors are David Avery and Harry Hey, and the Electrolytic Zinc Co. of Australasia, Proprietary, Ltd., have been interested. H. J. E. Hamilton, of Broken Hill, has also contributed.

In England, F. E. Elmore and the Chemical and Metallurgical Corpn., of London, have been very busy, paying particular attention to the complex ores of the Burma Corpn. Sulman and Pickard, H. S. Mackay, P. A. Mackay, J. J. Collins, J. Nelson, and M. C. White are also contributors to the advancement of the art.

In Germany, F. Krupp and A. Nathansohn have carried out research work.

In Canada, at Trail, B. C., the Consolidated Mining & Smelting Co. has done considerable work in treating the zinc-leaching plant residues and an important improvement has been patented by one of its men, W. H. Hannay.

In the United States, a plant is in operation by the Tintic Milling Co., of Silver City, Utah; another plant is in operation by the Tintic-Standard Mining Co., at Harold, Utah; fairly large test plants have been built and operated by the Bunker Hill & Sullivan Mining, Concentrating & Smelting Co., at Kellogg, Idaho (J. L. Malm, R. S. Handy, C. L. Larson, W. G. Woolf, and U. C. Tainton); by the Anaconda Copper Mining Co. at Great Falls, Mont. (J. O. Elton and R. B. Caples); the U. S. Smelting, Refining, and Mining Co. at Kennett, Calif. (H. R. Hanley). Smaller

scale experimental work has also been carried on by the Butte and Superior Mining Co. at Butte, Mont.; the Philipsburg Mining Co., at Philipsburg, Mont.; S. Ganelin of Brooklyn, N. Y.; N. C. Christensen, of Salt Lake City, Utah; Francis N. Flynn and G. D. Van Arsdale, of New York; P. R. Middleton, of New York; Robert DeLuce, of Oakland, Calif.; and others.

### *Spence Process*

One of the earliest attempts at treatment of lead ores by hydrometallurgical means was that of Spence, of England, reported by Collins.<sup>29</sup> Slime of a complex sulfide ore, containing 48 per cent. zinc and 14.7 per cent. lead, was treated with 100 gal. commercial muriatic acid per ton ore and the resulting lead chloride washed out with 12 tons hot water, leaving a residue containing 2 per cent. lead and 57.5 per cent. zinc. Two-thirds of the lead precipitated from the hot water on cooling and the remainder was recovered as lead-chromate pigment by adding chromates to the solution. This process was worked for several years but commercially was unsuccessful, the reasons for this, however, have not been stated.

### *Holt-Christensen Process*

Since 1914, mills in Utah have been using processes that grew out of the work of T. P. Holt and N. C. Christensen, all of which involved chloridizing roasting in blast roasters, followed by leaching with brine. Silver and copper have been the two metals sought but it has always been recognized that the brines were saturated with lead. Precipitation of the silver and copper has taken place on scrap iron and at the temperature of the mill solutions (20° to 35° C.) very little of the lead in the solution was precipitated. In fact, lead does not begin to precipitate until most of the silver and copper have been cemented on the iron. Intermittent attempts were made to develop a cheap way of recovering the lead, but it was not until the high prices of lead in 1922 and 1923 that any of the methods of precipitation that had been developed were adopted in practice. At present, that portion of the lead which happens to dissolve is recovered in the mills of the Tintic Milling Co. and of the Tintic-Standard Mining Co.

### *Tintic Standard Mill*

At Harold, Utah, in the eastern part of the Tintic district, the Tintic Standard Mining Co. is engaged in mining a large deposit of ore, part of which can be shipped directly to the smelters and part of which must be milled. Because of its oxidized condition, mechanical concentrating methods are not efficient and leaching methods have been adopted, using

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<sup>29</sup> H. F. Collins; "Metallurgy of Lead," 2d Ed., 491. C. Griffin & Co., London.

the Holt-Dern process as developed in the mill of the Tintic Milling Co. The ore has the following average partial analysis:

Au, ounces per ton.....	0.025	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> , per cent.....	16.3
Ag, ounces per ton.....	17.0	CaO, per cent.....	0.33
Cu, per cent.....	0.35	Zn, per cent.....	0.12
Pb, per cent.....	4.0	S, per cent.....	2.5
SiO <sub>2</sub> , per cent.....	56.0		

Two hundred tons of this ore are treated daily by pulverizing, mixing with coal dust and salt and then roasting in a blast roaster of the Holt-Dern type. This chloridized ore is then placed in wooden leaching vats and treated with a strong brine, which dissolves the silver, copper, gold, and lead. To get a good extraction of gold requires the use of a strongly oxidizing solution containing ferric chloride; but in this mill not enough gold is present to warrant the using of such solutions. A barren solution and a wash solution follow the original leaching solution in treating the ore. The metal extractions claimed, based on smelter settlements, are 82 per cent. silver, 40 per cent. copper, and 40 per cent. lead; steps are being taken to improve the lead practice on account of the value because of enhanced metal prices, as the roasted ore has 85 per cent. of the lead in brine-soluble form. The pregnant solution is pumped to towers where it passes the roasting gases and is thus acidulated with sulfuric, sulfurous, and hydrochloric acids from the roaster. It is then passed to the silver precipitators, where copper is used to displace the silver from solution. After this, the solution is run over scrap iron in launders, or long boxes, and the copper recovered. Then the solution is heated by live waste steam to 75° C. and passed to launders containing baled tinplate scrap from local canneries. One pound of iron precipitates 2.6 lb. of lead and the composition of the lead precipitate is as follows: silver, 2 to 5 oz. per ton; copper, 3 to 5 per cent.; lead, 78 to 83 per cent.; iron, 3 per cent.; insoluble, 3 per cent.; arsenic, 0.7 per cent.; and zinc, 0.7 per cent.

Heating the solution has the disadvantage that the steam dilutes it, thereby greatly reducing its lead dissolving powers. However, for ordinary dense iron, it is absolutely necessary to heat the solution to obtain a utilizable velocity of precipitation. Sponge iron was tried, being placed in the launders; while it functioned very well, the sponge lead clogged the precipitating trough and not all of the iron was used up. However, because of its success in the mill of the Tintic Milling Co., sponge iron is again being considered. Inasmuch as the lead has been a byproduct, recovered incidentally to the extraction of silver, the cost of recovery has merely been calculated on the precipitation and marketing expenses, neglecting a proportionate share of the grinding, roasting, and leaching; on this basis the lead cost 1.6 cents per lb. on cars ready for



shipment to a smelter. On this basis, the cost of extra plant for recovering the lead was amortized very quickly and the operation has been on a profitable basis ever since. By preparing a cleaner lead precipitate and smelting it into bars for direct sale to the lead consuming market, more would be realized than shipping the lead precipitate to a lead smelter merely as a rich-lead ore. Improvements both in extraction and grade of precipitate are being investigated and developments will be awaited with interest.

### *Plant of Tintic Milling Co.*

This was the first successful chloridizing, roasting, and leaching mill in the Tintic district and followed a similar mill built at Park City by Holt and Dern. It is located at Silver City, Utah, and has been treating oxidized ores from several mines of the Knight and Dern interests for nearly eight years. Its capacity is 200 tons daily but, recently, because of the dwindling ore supply, only about 100 tons daily have been treated, and the silver content is now only 7 or 8 oz. per ton. Present operation is therefore intermittent. The pulverized ore is mixed with coal dust, pyrite, and salt and blast-roasted in Holt-Dern shaft roasters. The gases from the roasters are passed up a scrubbing tower supplied with pregnant solution in order to give up any acid formed in the vapors, and thereby acidify the solution so that better precipitation of silver and copper can be obtained. The roasted ore is collected in round wooden leaching vats and treated first with a solution low in silver and other metals, and is then passed to precipitation. Then it receives a wash, by barren solution from the precipitation launders, and, finally, a water wash to recover salt. Since starting to recover the lead from them the solutions have been raised by the addition of salt from 22° Bé density to 27°, with a corresponding increase in the amount of lead from 4.7 to 10 gm. per liter, at ordinary temperatures. No attempt was made to purify the brines in order to increase their dissolving power for lead, nor has sufficient brine to extract all the lead been used.

The interesting part of the Tintic Milling Co. mill is the use of sponge iron for precipitation of the lead. Silver and copper are precipitated first on scrap iron, more or less as at the Tintic Standard Mill; then the solution passes to several long launders with false bottoms, on which a 4-in. layer of sponge iron is spread. Cold solutions are completely precipitated in passing slowly down through this layer of sponge iron. The sponge iron is made from a low-grade iron ore mined locally and containing small amounts of silver, which is mixed with an equal weight of coal slack and heated to about 950°–1000° C. in a continuous rotary kiln developed by the Northwest Experiment Station of the Bureau of Mines (Seattle). The coal prevents any reduced iron from reoxidizing and a small 27 by 3 ft. kiln is producing 3 tons of sponge iron daily (the

amount required by the mill) in which the iron oxide is from 80 to 98 per cent. reduced, depending on operating conditions. As iron in a lead ore is credited by the lead smelter, no attempt at complete reduction of the iron is made, nor at complete replacement of iron by lead during precipitation, so the resulting precipitate contains 20 per cent. iron and 40 to 60 per cent. lead, and a considerable amount of insoluble and other material from the original iron ore, nevertheless acceptable to the lead smelter. This successful commercial production of sponge iron came almost coincidentally with the production of 6 tons daily by the Chino Copper Co., by the Thornhill process, for purposes of copper precipitation. The use of sponge iron from lead precipitation had been experimented with, for a number of years, by others, notably, H. R. Hanley, at Kennett, Calif., in 1917 and 1918, but the Silver City work was the first attempt at commercial operation.

Just why sponge iron should be so efficient at ordinary temperature, in comparison with dense iron, is difficult to explain, unless it is because of the enormously multiplied surface exposed. Sponge iron functions fairly efficiently at 30° C., whereas dense iron, in the form of detinned light tin-plate scrap, requires at least 75° C.

#### *Bunker Hill & Sullivan Leaching Plant*

Some of the early research on the hydrometallurgy of lead originated at the Bunker Hill & Sullivan plant, in Kellogg, Idaho, and several years' work has been done. At first, the chlorination process of John L. Malm, intended mainly for the treatment of complex sulfide ores, was tested; but due to several operations for which mechanical apparatus had not been developed and to the simple silver-lead ore that was proposed for treatment, was later dropped. However, during this work it was discovered how easily galena could be sulfated either during oxidizing or chloridizing roasting and also that lead sulfate was soluble in strong brines. Later, the brine-leaching and electrolysis process developed by the Bureau of Mines at its Salt Lake experiment station was tested at Kellogg under the direction of C. L. Larson, who patented the sequence of operations that was successful.<sup>20</sup> The work of Larson showed that the silver and lead in the Bunker Hill ore should be extracted by chloridizing roasting, brine leaching, and electrolysis with iron anodes as cheaply as, or more cheaply than, by concentrating and smelting. However, before he had reached this conclusion it had become necessary for the company to build a smelter and shortly afterwards the test plant for lead leaching was burned. It was later rebuilt and Larson's work was continued by W. G. Woolf, another of the former Salt Lake experiment station

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<sup>20</sup> C. L. Larson: U. S. Patent No. 1284910, 1918.

men, who, however, began to test a modified process of U. C. Tainton, for which a 50-ton pilot plant was built and is now in operation. Details of Tainton's process are not available but doubtless will be published later.

In general, the process is to roast the simple galena ore (80 to 95 per cent. gangue) in an electrically heated roaster designed by Tainton, that is expected to expend 30–50 kw.-hr. per ton of ore, heated to 500° C., at which temperature all of the galena is converted to lead sulfate. A water wash will remove soluble sulfates of manganese, magnesium, and other metals and thus diminish fouling of the brine solution which follows. The brine is saturated with salt and contains dissolved chlorine from the electrolytic cells, the purpose of the chlorine being to attack any unroasted galena but mainly to take silver compounds into solution as silver chloride. The brine is applied in agitators, thickeners, and a wood-lined Burt filter, which allows piston displacement of the brine from the filter cake by water. Calcium chloride is introduced in amounts sufficient to precipitate all sulfates from solution as calcium sulfate and prevent fouling of the solution. The lead and silver are precipitated from the brine in an electrolytic cell with rotating sheet-iron cathodes enclosed in a wooden-frame filter-press type of electrolytic cell with graphite anodes enclosed between wooden diaphragms of veneer. The sponge lead does not adhere to the cathodes but floats out of the cell with the brine and is collected and pressed into cakes ready for melting. The chlorine collected in the anode compartments dissolves, in part, in the solution and the remainder is absorbed in a lime scrubbing tower, producing calcium chloride and hypochlorite for returning to the circuit, as mentioned above. It makes possible 90 to 95 per cent. extraction of the silver and 95 to 98 per cent. of the lead, without the necessity of a chloridizing roast. This is an important contribution to the subject. It is expected that the huge accumulation of tailing from the lead concentrating mill will be treated economically and also that the process can be modified to treat the tailing from an electrolytic-zinc plant soon to be built.

#### *Process of F. N. Flynn*

F. N. Flynn, in conjunction with G. D. Van Arsdale,<sup>31</sup> patented a process for treating products containing lead sulfate and was actively engaged in promoting a modified brine-leaching-and-electrolysis process in which a diaphragm cell was used and ferric chloride was formed at the anodes, with simultaneous depolarizing of the anodes.<sup>32</sup> This ferric chloride was reduced to ferrous chloride by the addition of calcium-sulfite liquor made outside of the circuit. Enough lime was also added to precipitate any excess of iron that accumulated in the solution, and to remove sulfates resulting from the dissolution of the lead sulfate. The lead-

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<sup>31</sup>F. N. Flynn and G. D. Van Arsdale: *Loc. cit.* <sup>32</sup>See discussion on p. 468.

sulfate material or ore was merely treated with a sodium-chloride brine containing ferrous chloride. The ferric chloride was not utilized for its oxidizing power on any lead or silver minerals. Therefore, the process was of value principally for recovering lead and probably of little value for silver-bearing materials, except where the silver had already been converted to brine-soluble form.

### *Experiments on Kennett Zinc-plant Residue*

Early in 1918, the U. S. Smelting Refining & Mining Co. carried out tests of brine leaching of their electrolytic-zinc plant residue at Kennett, Calif., which had the following average analysis: 0.68 per cent. Bi, 1.3 per cent. Cu, 11.92 per cent. Pb, 8.3 per cent. Zn, 0.35 per cent. Cd, 9.7 per cent. Fe, 6.5 per cent. S, 4.4 per cent. CaO, 27.1 per cent. water, 0.05 oz. Au and 6.3 oz. Ag per ton. This work was under the direction of H. R. Hanley. It was found that 85 to 86 per cent. of the bismuth, 90 to 94 per cent. of the lead, and 40 to 50 per cent. of the silver dissolved directly in the acidified brine. A brine-leaching section to the plant was never built, as the plant was later closed on account of the unfavorable zinc market. Sponge iron was found to be an efficient precipitant of the lead. Precipitation on scrap iron was complete only after two hours tumbling of the solution and iron in a barrel and was discarded as non-commercial.

### *Semicommercial Plant at Trail, B. C.*

Late in 1918, the Consolidated Mining & Smelting Co., at Trail, B. C., built a semicommercial test plant for treating tailing from its electrolytic-zinc plant. It was constructed near the tailing heap and also contiguous to the electrolytic-lead refinery so that the brine, after being loaded with lead, could be run to cells in the refinery and the lead recovered. About 15 tons of zinc-plant residue were treated daily and about \$25,000 was spent in testing the process. Brine leaching, followed by electrolytic precipitation with cast-iron anodes weighing 500 lb. each, was the process tested. Wooden tanks and pipe were used and caused considerable trouble from leakage when the wood was shrunk by the warm brines. The technical aspects of the process were very satisfactory, as practically all the lead in the material and much of the silver could be dissolved; but it was determined that the process would be more economical than smelting only when the residue contained less than 18 to 20 per cent. lead, whereas the zinc plant residue at that time contained 24 per cent. lead. The residue, therefore, is still being treated in the lead blast furnaces.

The solid material was pulped with brine in a mechanically agitated tank (air agitation was avoided as a warm solution was desired) and

solution of lead and silver was effected in 45 min. With a neutral brine, most of the lead, but only 50 per cent. of the silver, dissolved. By adding 1 to 2 gm. sulfuric acid per liter, the silver extraction could be increased to 78 per cent. For over a month, early in 1919, the plant was in excellent running order and made a 93.8 per cent. extraction of lead and 75.8 per cent. extraction of silver. The leached mixture was then run from the batch agitator to a 40-ft. Dorr thickener, where about 50 sq. ft. of settling surface per ton solids per 24 hr. was found necessary. The overflow contained 9 to 10 gm. lead and 1 to 2 gm. sulfuric acid per liter. Silver was precipitated with scrap iron contained in launders and the resulting brine was then pumped to the electrolytic plant. The settled slime from the Dorr tanks was filtered in American disk filters without much washing, so that brine containing 150 lb. of salt was left in each ton of residue.

In the electrolytic-tank room concrete cells 7 ft. 3 in. long by 2 ft. 6 in. wide, and 5 ft. deep were utilized, leaving room below for a loose porous bottom through which air could be introduced to shake the sponge lead off the cathodes, 25 to 30 cu. ft. air per min. being blown in. Iron anodes and cathodes were used, spaced 1.5 in. apart and with a current density of 15 amp. per sq. ft. the potential drop was 1.0 to 1.5 volt. From 12 to 15 lb. of lead were precipitated per kilowatt-hour electric energy expended and iron consumption was 0.3 lb. per pound lead. Each cell produced 250 lb. lead per 24 hr. The sponge lead was best handled by briquetting and melting. The tail solution from the cells contained 2 gm. lead per liter, and was returned to the leaching plant.

An analysis of the solution after fourteen cycles showed 191 gm. chlorine per liter, 27 gm. iron, 62 gm. sulfur (as sulfates), 2.3 gm. lead, and 5 gm. zinc. It was then purified by addition of milk of lime, leaving 154 gm. chlorine, 9.6 gm. sulfate, trace iron, trace lead, and trace zinc. Concrete construction seemed to be preferable to wood, as it did not shrink. Total costs of operation per ton, including the salt loss, were expected to be slightly less than \$5 on 15 per cent. lead material.

### *Great Falls Experiments*

Late in 1919, the Anaconda Copper Mining Co. tested the same process for treating the electrolytic-zinc plant residue. Practically, the same conditions as had been used at the Salt Lake experiment station were adhered to. Suitable apparatus was set up in the old electrolytic-copper refinery in order to have electrolytic tanks for recovery of the lead. The normal zinc-plant residue contains 14 per cent. zinc, 12.3 per cent. lead, and 25 per cent. water but the material available at the time contained over 40 per cent. water and seriously diluted the brine. Leaks and the absence of suitable filtering equipment caused the use

merely of settling tanks to separate the solution from the ore, followed by repulping with wash water; the loss of salt under these conditions was 318 lb. per ton. From 14 to 15 hr. of settling gave a clear overflow liquor.

In all, about 7788 lb. of lead sponge was recovered, representing a recovery of 93.7 per cent. of the original lead; 60 per cent. of the silver was soluble in neutral brine, and 90 per cent. in acidified brine. The sponge lead contained 25 per cent. moisture, as removed from the cells, and only 62 per cent. lead. It was melted without briquetting, giving about one half the lead as molten metal and the other half was drossed. The melted lead contained 0.83 per cent. copper, 0.02 per cent. iron, 0.15 per cent. zinc, 26.2 oz. silver per ton, and 0.08 oz. gold. Evidently, briquetting of the sponge lead is essential to satisfactory melting.

Batch agitation was practiced, a Pachuca agitator being filled with about 8 tons of brine containing 300 gm. sodium chloride per liter and then enough ore added so that 1 ton of solution was present for each 20 lb. of lead to be dissolved, this being from 1400 to 2300 lb. of zinc-plant residue. Agitation was continued for 30 min. after the addition of all the material. The batch was then transferred to settling tanks by a sand pump and the clear liquor fed direct to the electrolytic cells, of which there were four (old copper-refining cells) placed in cascades of two each, about 9 ft. 6 in. long, 2 ft. 3 in. wide, and 5 ft. deep with a false bottom of canvas to provide agitation by air. Anodes and cathodes were  $\frac{1}{2}$ -in. iron plates supported by copper rods. The electrolyte flow was about 2 gal. per min. for each 1000 amp. and a yield of lead amounting to 14.74 lb. per kw.-hr. energy was obtained while 2.5 lb. lead precipitated during the solution of 1 lb. iron at the anode. Experience showed it best to provide solution containing about 10 gm. lead per liter, which could be reduced easily to 2 gm. during passage through the cells. Occasional removal of accumulated zinc, iron, and sulfates by the addition of lime was advisable.

It had been planned to use enough zinc dust to precipitate all copper and silver at the end of the leaching and then to smelt the residue in a reverberatory furnace for the production of copper matte. Previously, the residue had been shipped to the lead smelter at Tooele, Utah. The data on brine leaching, followed by matte smelting at Great Falls, showed a saving over shipping to the lead smelter at Tooele, but later the lead smelter at East Helena, Mont., offered such advantageous smelting rates, in order to get this leady material for mixing with other ores, that work on brine leaching was abandoned.

The conclusion about brine leaching at Great Falls was that very few difficulties were apparent but that evaporation of wash solution for recovery of salt would probably be necessary; a very low cost of treatment was anticipated.

*Elmore Processes*

F. E. Elmore, of Boxmoor, England, has been engaged in developing numerous brine leaching processes for removing silver and lead from complex sulfide ores, especially having in mind the ore of the Burma Corp'n., small testing plants having been operated in London and at the mines in Burma. However, the isolated position of the Burma mines and the type of labor available there seem to discourage the use of chemical processes. Elmore's patents give a fair idea of his various processes. One method proposes dissolving the lead and part of the silver in hot saturated brines, which have been acidified. Hot brines containing acid or ferric or cupric salts have also been used by many other investigators and have been shown to be efficient solvents of lead sulfide but frequently will not attack the sulfide minerals of silver efficiently without also attacking the zinc sulfide.

Another of Elmore's processes involves treatment of the mixed sulfide ore with concentrated sulfuric acid at about 100° C. in order to attack the galena and convert it into lead sulfate, which can later be removed with a brine, together with any silver that yields to such treatment. However, his patents give few details of results obtainable. Fortunately, a few tests on this method were made at the plant of the Butte & Superior Mining Co. When treating the regular concentrate of the mill in a small laboratory test, material containing 55.8 per cent. zinc and 4.1 per cent. lead was heated for 2 hr. at 100° C. with 1.84 sp. gr. sulfuric acid (94 per cent.). This was then poured off, washed with water, and a hot saturated brine used for removing the lead. The final residue weighed 89.7 per cent. of the original and contained 1.85 per cent. lead and only 52.6 per cent. zinc. While much of the lead was removed, the loss of zinc was regarded as prejudicial to the process. A sample of middling from the mill was also tested. It contained 10.9 per cent. lead, 27.1 per cent. zinc, 19.1 per cent. iron, and 16.6 oz. of silver per ton before treatment. After treatment, it had lost 22 per cent. in weight, contained 20.6 per cent. zinc, 1.80 per cent. lead, 23.1 per cent. iron, and 20.6 oz. silver per ton. Again, too much of the zinc was attacked.

The Christensen processes (*loc. cit.*) resemble the Elmore processes very much except that most of Christensen's proposals involve the use of sulfuric acid in varying concentrations and heating until the zinc sulfide is also converted to zinc sulfate, which is soluble in strong sulfuric acid and can be recovered from it. Brine leaching of the lead and silver from the decomposed residue is then possible. The Anaconda Copper Co. also carried out experiments on "fuming" mixed sulfide ore with sulfuric acid and found it possible to decompose it completely so that the zinc could be leached out separately, followed by brine leaching of the lead and silver; but it decided against the method on account of mechan-

ical and other difficulties. If complete decomposition of the ore is carried out in place of the partial sulfating attempted in some of the foregoing processes, the principal advantage is the possibility of practically a complete recovery of the valuable metals while the mechanical and chemical difficulties are not insurmountable and the economics of the method should be capable of satisfactory adjustment by careful design. More work along these lines, or discussion from those who have already carried out such tests, is desirable.

### *Amalgamated Zinc (DeBavay's) Ltd. Processes*

This Australian company has been developing what seems like one of the most practical of the numerous schemes proposed for removing lead and silver from zinc-sulfide concentrate without having to decompose the zinc sulfide. The ore is mixed with sufficient zinc chloride to supply 33 per cent. excess chlorine over that necessary for combining with the lead, silver, arsenic, antimony, and tin in the ore and heated to 400°–500° C. with agitation out of contact with air, presumably in a muffle. Under these conditions, the zinc chloride exchanges its chlorine with the other metals present. Chlorides of arsenic, antimony, and tin are volatilized and chlorides of lead and silver are formed but remain in the anhydrous mass. It is then cooled and washed with acidulated water to remove excess zinc chloride, followed by brines to dissolve the lead and silver. Because of the tendency of silver to reprecipitate on zinc sulfide, it is necessary to use a brine containing hydrochloric acid, ferric chloride, or cupric chloride, preferably ferric chloride, and to give this solution a minimum time of contact with the ore. The silver can be removed by a cold brine saturated with lead chloride and containing ferric chloride before the lead is removed by a barren hot brine. A cold solution is used for this purpose in order to minimize the action between zinc-sulfide particles and the ferric chloride in solution. One of the patents of Harry Hey gives details of some of the tests made by this company. A series of 66 charges of ore, totaling about 9 tons of Broken Hill zinc concentrate, was chloridized by the above method and then treated in a leaching vat about 3 ft. deep with the following series of leaching solutions, applied so that they went immediately through the charge and did not soak:

- (1) For each 300 lb. batch of ore, 10 gal. water with 0.013 lb. HCl per gal. (1.3 gm. per liter) to remove excess zinc chloride.
- (2) 60 gal. cold brine (24 per cent. NaCl) containing lead chloride and 0.03 lb. HCl per gal. to remove silver (as chloride).
- (3) 60 gal. neutral brine (24 per cent.) at 90° C. to remove lead (as chloride).
- (4) 10 gal. of water to recover salt.

The original ore contained 6 per cent. lead, 48 per cent. zinc, and 7.7 oz. silver per ton. The final residue contained 0.21 per cent. lead,



52 per cent. zinc, and 0.7 oz. silver. This is probably one of the most promising and practical of the more recently designed applications of brine leaching of lead. It would depend on the ability to prepare cheap zinc chloride and also solutions of brine containing ferric chloride or hydrochloric acid in small amounts. There is reasonable possibility of doing both of these things economically.

## DISCUSSION

F. L. BOSQUI, JR., Kellogg, Ida. (written discussion).—Having been directly connected with the recent brine-leaching work at the Bunker Hill & Sullivan mine in Kellogg and, also, having made a special study of the literature of this subject, the writer finds this paper of great interest. On account of the author's position in the Bureau of Mines, which has initiated such valuable research work on the hydrometallurgy of lead, his description of the basic principles involved, and of the large-scale operations developed on these principles, is most instructive. But we are surprised by his statement that "a number of commercial plants are in operation" and wish that he had given more information about these.

Apart from the new plant at Kellogg, there is at the present time, so far as we know, only one commercial brine-leaching plant in operation: that of the Tintic Standard Mining Co., in Utah. As the author has pointed out, however, the recovery of lead in this case is quite incidental to the main operation, which, in the last analysis, appears to be a rejuvenation of the old Augustine process. In fact, we are told that only "that portion of the lead which happens to dissolve is recovered," and that the product, carrying a considerable proportion of iron and other impurities, requires smelter treatment. The process can, therefore, hardly be considered one of true hydrometallurgy.

It is true that the subject of lead leaching has been carefully investigated, and several test plants have been erected and operated by some of the large mining companies; but it is also true that in every case the work was abandoned and the plants dismantled. Obviously, the degree of successful commercial operation attained is a question of real importance. The facts seem to indicate some inherent weakness in the methods used; they also show that the hydrometallurgy of lead has not become generally accepted as a practical process. The author would appear to convey the opposite impression, and to minimize the serious obstacles that this method of treatment has encountered, presenting problems, some of which, one might venture to say, remained unsolved in spite of a great amount of experimental work. Perhaps the most serious of these, from an economic standpoint, has been the extraction of the silver. On account of the widespread occurrence of the so-called silver-lead, and

"complex," ores, the silver recovery becomes a particularly important factor if the method would compete with smelting practice.

The use of acidified brine, on which so much reliance has been placed in connection with silver extraction, is, in the case of many ores, quite ineffective. We have in mind especially certain zinc-plant residues where acidified brine yielded only 5 per cent. of the silver. After chloridizing, an extraction of 85 per cent. may be obtained on some ores, but in the case of those that are oxidized, the silver extractions possible by this method are often less than 50 per cent.

Only recently has the importance of a strongly oxidizing, rather than an acid, solution been recognized; but, because of the methods of precipitation employed, it has hitherto been impossible to take advantage of such a solution in cyclic operation.

The precipitation of the lead has involved the use of iron, either as a direct precipitant or in the form of soluble anodes (disregarding chemical precipitation, which has never been used on a large scale). That the cost of this iron is a considerable item may be judged from the fact that its consumption is chemically equivalent to the amount of lead precipitated. The resulting accumulation of iron in solution must be got rid of, and the only method so far proposed involves its precipitation in the pulp in the form of a hydrate. This is a substance that is difficult to settle and filter in dense solutions. When it is recalled that the volumes of solution to be handled are very large (1 ton of lead requires at least 100 tons of solution) it can be readily understood how serious are the leaching problems connected with this operation. Furthermore, the iron is introduced into circuit in the ferrous state, and the ore is leached with a solution that is essentially reduced—a condition that is most unfavorable to the recovery of silver, as was pointed out above.

The soluble anode cell thus inevitably involves the iron difficulty. In addition, it is difficult to prevent the formation of light, spongy lead. This porous, floating material is notoriously difficult to wash, briquette, and melt. In fact, it was largely on account of the unpromising nature of this problem that the Bunker Hill & Sullivan Mining Co. abandoned, in 1917, the work it was carrying out in conjunction with the Salt Lake City Station of the Bureau of Mines. In attempts to use the insoluble anode cell, the problems of effective diaphragms and satisfactory chlorine disposal were not solved; also, on account of the low concentration of lead in solution, the low current efficiencies obtained discouraged the work in this direction.

These hydrometallurgical problems have been attacked afresh, however, by the Bunker Hill & Sullivan Mining Co., and the methods developed by U. C. Tainton give promise of eliminating the major difficulties. It is too early, however, to make any definite statements on the subject. Indeed, the information about this work contained in this paper

is a surprise to us, especially as the account, both in regard to the development of the process and its actual operation, is incorrect in several particulars.

It must not be supposed that it has been our purpose to belittle the real value of the extensive experimental work carried out in the field of lead leaching; nor do we take a pessimistic view of future developments, for we look forward to the widespread adoption of this form of treatment. The point we would stress is that the proposed methods, such as the author has described, did not culminate in commercially successful plants, and we have indicated some of the serious difficulties encountered.

It would seem, also, that a distinction should be drawn between the methods of treatment advanced. Those cases where the product requires actual smelting before it is obtained in a marketable form should be regarded as concentrating, rather than recovery, processes; and the costs in such cases should properly be compared with milling costs alone. The operations of the Tintic Standard Mining Co. are of this nature; and in regard to this one successful undertaking, it may be mentioned that the Salt Lake locality offers special advantages, such as the cheapness of salt and the close proximity to competitive smelters, which have permitted the sidestepping of many of the difficulties which would have to be overcome elsewhere.

GEORGE D. VAN ARSDALE, Los Angeles, Calif. (written discussion).—In the portion of the paper referring to the lead leaching and precipitation process of F. N. Flynn and myself there are one or two errors and statements possibly open to misunderstanding. It is of course difficult in such a complete paper to avoid occasional slips in detail, and the corrections to be made have been sent to the author and acknowledged as valid. They are brought into this discussion merely as a matter of record.

Reference is made, on page 460, to the process of F. N. Flynn; we are both equally concerned in the method. Mr. Flynn, several years ago, brought to my attention the difficulty he had experienced in treating products carrying lead sulfate. It occurred to me that some of the principles being applied in modern copper leaching could be applied also to the brine leaching of lead, and we together devised the method on which U. S. Pat. 1448923 was granted. Certain proposed applications of the method were described by Mr. Flynn in the article referred to in the paper.

The statement that we propose to use a diaphragm cell is not true. Calcium sulfite or lime are to be used only when ores being treated carry soluble iron in sufficient amounts to accumulate. When this is not the case, or when the ores carry sufficient lead in the form of sulfide, a ferric-iron balance can be maintained without the use of this reducing reagent. When the materials being treated carry considerable amounts of lead as

sulfate, free acid will accumulate if the ores do not carry enough lime to neutralize this, in which case the addition of lime to neutralize and precipitate such excess acid as calcium sulfate becomes necessary. The lead sulfate or ore is not treated with a brine carrying ferrous chloride but with one carrying ferric chloride, where useful solvent effect can be had from this ferric salt, which of course results from the electrolysis of the solutions carrying ferrous iron. Obviously, therefore, such ferric chloride may be utilized for its solvent action both on lead sulfide and such silver compounds as are acted on by it. It is, I believe, not correct to say that the process will probably be of little value for silver-bearing materials, except where the silver had already been converted into brine-soluble form. Naturally no general statement can be made as to action on all silver compounds, but I have proved that our solutions act efficiently to remove the silver from the lead ores I have tested so far. Judging from experience in other lines of electrolysis, I do not expect any difficulty in making ferric iron electrolytically in sufficient concentration to act as an active solvent, and at the same time not reduce the cathode efficiency below a commercial figure. Methods of doing this, and of controlling the balance of ferric and total iron, will naturally vary to a considerable extent with the conditions imposed with the ore, etc. being treated. These are important details on which a considerable amount of work has been done, but hardly necessary to describe here.

It appears to be certain, as stated in the paper, that a definite field of usefulness has developed for the brine-leaching treatment of lead ores and other products. Precisely as with copper leaching, dissolving is a comparatively simple matter, and it is only when we come to methods of separating the products and regenerating our solvents that we encounter much difficulty. We can look for more rapid progress in the development of lead hydrometallurgy than has been the case with that of copper, for we have developed more or less standard apparatus, which was not the case in the early days of copper leaching. There is a certain amount of parallelism in the two problems in that chemical and electrolytic methods are available for both. What we can call chemical methods, including iron precipitation, have certain advantages, but they will not survive in competition with electrolytic methods for either copper or lead. Precipitation of copper by iron, generally speaking, costs more than electrolysis, and I think that the same thing will prove true with lead, particularly as heating seems to be required for iron precipitation of lead, except when sponge iron is used. The economical making and use of sponge iron depends, to a considerable extent, on cheap fuel and source of the raw material for making it, while with electrolysis, cheap power only is required.

The electrolytic method of lead precipitation developed by the Bureau of Mines, involving the use of soluble iron anodes, has the considerable

advantage of a low voltage and large yields of lead per kilowatt-hour at comparatively high current densities and consequent low tank-room cost. However, the iron consumed in the form of the sheet used as anodes, which will be quite expensive, must be charged against this, together with the scrap from partly consumed anodes. As low voltages can be had also with an insoluble anode (graphite) under proper conditions of depolarization, this method has also the advantage of quite a satisfactory yield of lead, in pounds per kilowatt-hour. The production of lead in the form of sponge seems to be a disadvantage that is common to all the electrolytic methods so far proposed as well as to iron precipitation. It is to be hoped that further research will develop a method of electrolytically depositing reguline lead from these solutions.

A method for direct leaching of lead ores carrying part or all of their metal content as sulfide, without roasting either by a sulfating or chloridizing roast would eliminate this operation which, in some cases, will amount to a considerable charge. A considerable amount of work has been done on leaching direct without roasting some forms of copper sulfides, and it is perhaps not too much to hope that research may develop a method by which the same may be done for lead.

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## Present Trend in Treatment of Complex Ores\*

BY G. L. OLDRIGHT,† SALT LAKE CITY, UTAH

NEARLY all of the present schemes for treating complex (*i. e.* lead-silver-zinc-copper) ores are based on the idea that lead holds, and will hold for some time, the strongest economic place from the viewpoint of supply and demand of all the non-ferrous metals. Copper, it is thought, will come back to its own when European affairs are stabilized, although at that time competition from Chile, Peru, and Katanga, in particular, will be more severe than in pre-war days. The future for silver and for zinc is uncertain. New uses are developing for zinc, and the market has remained better than many expected, but the stabilization of world markets will bring in foreign competition instead of relief.

The cost of producing zinc from simple zinc ores, by the retort process, will, from the nature of the labor required and the increasing cost of fuel, increase steadily. As a result, the small producers of purely zinc ores around Joplin are shutting down their mines, even with a good market price for zinc; on the other hand, the producer of lead from complex ores, in the Rocky Mountain states, is confident of a profit from the sale of his lead, and is seeking means to make the zinc in his ore pay some part of the cost of treatment. However, the tonnage costs for mining and ore dressing are much higher in the Rocky Mountain states, as may be seen by comparing tax-return statements from the various states. Even before the recent drop in the price of silver, many mines were operating on a very slender margin of profit; labor and supplies cost more. Mining at greater depth has shown most orebodies to grow increasingly more complex, so that improvements in mining and ore-dressing practice have not been sufficient to compensate for the additional expense involved in beneficiating these ores. The smelters have had to meet the same general economic situation, so they can only give

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\* By permission of Director of Bureau of Mines.

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### *Smelting-slag Constituents*

The next major operation in the treatment of the ore is smelting in the blast furnace. Here again the treatment, freight charges, and penalties for impurities are on a tonnage basis, emphasizing the importance of concentration. There are two materials, besides sulfur and speiss, for which penalties are exacted—silica and zinc.

### *Silica*

The desirability of silica as a constituent of the ore depends largely on the location of the smelter and the nature of the majority of the ores in the mines that supply it. At present, the average lead smelter has an excess of silica and is deficient in bases, such as iron and lime, which combine with the silica to form the slag; hence the bases are at a premium and the silica is at a discount.

With the increasing practice of concentration by flotation, as the mines go to greater depth, and the ores become more complex and less oxidized, the roles of silica versus bases may become reversed, in which case silica will be paid for. At present, however, the oxidized ores (which as a rule suffer large losses in valuable minerals by gravity concentration) are heavily penalized for their silica content. The problem of "excess silica" is, then, largely one of trying to remove the silica by concentration in such a way that the losses in metal values will not overbalance the benefit gained.

### *Flotation of Oxidized Ores*

The technique of the treatment of oxidized ores by flotation is not yet well worked out. The present developments appear to favor the use of an alkaline circuit, and as yet no schemes have been devised that have dispensed with the use of sulfidizing agents (such as sulfur, hydrogen sulfide, sodium sulfide, calcium sulfide, and poly-sulfides) to form a sulfide film around the oxidized particle to be floated. For instance, one company floating a partly oxidized copper ore has found it effective to use 0.2 lb. soda ash, 2 lb. sodium sulfide,  $1\frac{1}{2}$  lb. Barrett No. 4 oil, with a little soda resin solution (3 parts of resin boiled in a solution containing 1 part of caustic soda) per ton of ore. On another ore, a solution of equal parts of caustic soda, sulfur, and soda ash with a little Genasco or Barrett No. 4 oil, was found to give good results. For some oxidized lead ores, a mixture of paraffin and sodium sulfide ground in a mill with a little oil, like Genasco 250, has been used effectively. Fatty organic acids have been tried. Like the rest of the field covered by flotation, important developments are looked for which would be greatly accelerated if a more comprehensive theory covering the subject could be formulated.

## TREATMENT OF COMPLEX SEMI-OXIDIZED ORES TOO LOW-GRADE TO BE SMELTED

From a glance at the treatment cost sheet, it is evident that a highly siliceous, low-grade, oxidized lead ore that cannot be successfully concentrated cannot be sold to the smelter on advantageous terms. In fact, some smelters will not pay for any of the lead if it is under 4.5 or 5.5 per cent. In order to meet the demands exacted by smelters for this type of ore, some modifications have been made to the Holt-Dern (or Knight-Christensen) brine leaching process,<sup>2</sup> which make it possible to extract the lead as well as the silver and copper.

*Brine Leaching*

Briefly, in this process the low-grade, semi-oxidized ore that contains, in order of value, minerals of silver, lead, zinc, and copper, is treated as follows: The ore is crushed to about 75 per cent. through 20 mesh, and there are added about 3 per cent. coal (varying with the amount of sulfur, which preferably should be present) 7 per cent. salt, and (as in Dwight-Lloyd practice) enough moisture so that the product will cake when pressed in the hand. The Holt-Dern furnace, in which the ore is roasted, is an updraft blast roaster with a rocking-grate bottom which enables the calcines to be readily discharged. It handles about 20 tons of ore per day, gives a sandy, crumbly product, and is operated so that a temperature of 700° or 800° C. is maintained in the center of the charge.

After roasting, the ore is leached with a series of nearly saturated brine solutions, some of which are faintly acidulated by showering through the roaster gas in the flue. The total cycle takes five days. From the first solution off (the pregnant solution), the silver dissolved is precipitated on copper, the copper on coarse scrap iron, and the lead, from hot solution, on light detinned scrap iron, or, from cold solution, on sponge iron. The zinc at present is lost. (It may be precipitated by milk of lime, but too many other bases are precipitated with it.) From present developments, it would appear that this process extracts from 80 to 90 per cent of the lead, silver, and copper, each obtained as a separate fairly pure bullion. The process is most successfully operated at the plant of the Tintic Standard Co. at Harold, Utah.

*Direct Volatilization*

The volatilization process has been devised<sup>3</sup> for a similar type of ore, which contains lime as well as silica. The Chief Consolidated Co. is soon to erect a volatilization plant at Eureka, Utah. Judging from

<sup>2</sup> T. P. Holt: Chloridizing Leaching at Park City. *Trans.* (1914) 49, 183; *Innovations in the Metallurgy of Lead.* U. S. Bureau of Mines *Bull.* 157.

<sup>3</sup> Bureau of Mines *Bull.* 211.



present tests, it will recover the lead nearly completely, about 90 per cent. of the silver, but will leave the small amount of copper and zinc in the tailing. The ore will be treated by volatilization in a kiln, similar to those used for clinking cement, and the volatilized product caught in bags and shipped as a concentrate to the smelter.

### *Present Payment Made by the Smelters for Metals in Complex Ores*

Before going into the processes recently developed for the elimination of zinc, which is the most heavily penalized impurity, it may be well to note a few of the credit items on the cost sheets, and to see how the payments made by the smelter fit in with other metallurgical processes.

It should be frankly stated that many of the deductions made by the smelter from the market price of the metals, or from their content in the ore, do not represent metallurgical losses, but allow the smelter some leeway on fixing a "treatment charge." If the smelters paid for all the metals they extracted the treatment charge plus their profit would lie between \$10 and \$14. The shipper is accustomed through long experience to accept a nominal treatment charge, so the smelter gives it to him and withholds a corresponding value from the metals he actually recovers. Also, the smelter may take ores from a low-grade ore district at "under" cost, and have a clause in the contracts on high-grade ores that permits an "absorption of X per cent. over \$Y per ton" to make up for the loss.

The following sound deductions, however, may be made: The subtracting of, say,  $2\frac{1}{2}$  c. from the market price of copper, or 1.65 c. from the market price of lead is made to cover a "freight and refining" charge to take the metal east and to refine it. As the markets are mostly in the East, the freight charge is not objectionable; but if a small operator, capable of producing a fairly pure bullion containing only a slight amount of precious metals, desires to avoid the refining charge he should attempt to develop a local market for his product and not sell it to the smelter. (A large producer in the West would have considerable difficulty in disposing of his product in a local market.) A flat deduction, of course, makes a much higher percentage deduction on a low-grade than on a high-grade ore. As charges are also made, on a tonnage basis, for sampling, unloading, treatment, freight, and impurities, the mine operator must concentrate his ore. (The amount of raw ore of poor grade still being smelted directly justifies the emphasis placed on this step.)

As a whole, the lead and precious metals are fairly well paid for, zinc is penalized heavily, and a substantial deduction is made from the market price of copper. From these prices alone, taken into consideration with the fact that the smelters are bidding for ores in competition with each other, it is evident that lead and silver go with each other naturally,

that copper may be separated from the lead, but at considerable extra expense, while the zinc which is slagged off is not only lost, but involves an extra cost. According to the old dictum, "Zinc is what makes a complex ore complex."

From the smelter's standpoint, the presence of copper in a lead ore necessitates (roughly) the production of a matte in the blast furnace and an extra converting operation to remove any lead that enters the matte.<sup>4</sup> More zinc necessitates: (1) Forming a type of slag that requires a larger quantity of expensive iron flux; (2) in a siliceous district, more slag per ton of marginal ore; (3) more metal losses on account of more slag; (4) increased losses of copper, lead, and silver per ton of slag; and (5) because of the nature of the slag, furnace campaigns are shortened and troubles are increased.

As to the future savings that the smelter itself may make, the installing of more and better dust- and fume-collecting apparatus will undoubtedly save much of the metal loss in the smelter gases. Considering slag losses in general, where the losses are the result of chemical combinations, they may be prevented by causing the metal in question to assume some other chemical combination (*e. g.* the losses in copper when "black copper" was produced in blast furnaces, were afterwards prevented by making a matte). There seems to be an irreducible minimum amount of the metal in the slag, however, that is in solution or is retained mechanically. (It is said that the larger portion of lead lost in the blast-furnace slag escapes as lead silicate.)

It would seem logical that, in order to procure a larger immediate net return, it would be better to remove most of the valuable metals from a low-grade ore by concentration, and to leave the remainder in a carefully arranged tailing pile for future treatment, rather than to leave a greater total amount of the metals in the more difficultly treatable smelter slags.

### *Removal of Zinc*

The various lead-zinc-copper (the latter usually is present in smallest amount) mineral products made from ores may be conveniently divided, according to the amount of zinc they contain, into three classes: a high-grade zinc concentrate containing a small amount of lead (say from 3 to 10 per cent.); a zinc-iron-lead middling product containing the three metals in approximately equal amounts; and a high-grade lead product containing from 3 to 14 per cent. zinc. These three products usually, but not always, are obtained by concentration.

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<sup>4</sup> O. M. Kuchs: Lead-matte Converting at Tooele. *Trans.* (1914) 49, 579-584.

With the present costs, hydro-electrolytic processes for treating lead ores, such as leaching followed by electrolytic or chemical precipitation, do not compete with the smelter on the handling of high-grade lead products. For this reason, most of the hydrometallurgical processes have been developed for the treatment of the other two products mentioned—the high-grade zinc concentrate containing a little lead and the middling product containing zinc, iron, and lead. The retort and electrolytic plants are in competition for the zinc concentrate. It cannot be said that any satisfactory commercial process exists at present for the middling product, which is increasing rapidly in amount as the mines go deeper. Although in some mills this product is formed during flotation, a great effort is being made to eliminate it altogether and to make of it both a zinc and a lead concentrate.

### *Flotation*

Another characteristic that makes an ore complex is the intimate association of the minerals, so that concentration by gravity does not separate them—it is thought that some of the minerals that cannot be concentrated are chemically combined.

Anticipating the expiration of the principal flotation patent, there has been a rush to get patents on specific reagents that act preferentially, or differentially, on the various minerals. Enough success has been obtained for the more optimistic of the flotation men to believe that they will soon be able to separate almost any complex of minerals. For instance, although Dana describes marmatite as a zinc-sulfide mineral containing from a few tenths to 18 per cent. iron, some flotation men think that much of it may be only an extremely intimate admixture of blende, pyrite, and (possibly) chalcopyrite. Without varying the amount of oil added to the feed to a series of flotation machines, but by simply adding sulfuric acid at the head ends of some of the successive boxes, a decided preferential action may take place, and successive products floated that consist, for the larger part, of some one mineral. At present, the alkaline circuit is being favored. J. M. Callow's organization has developed a series of soluble products from coal tars, such as "x cake" "x.y.z. mixture," and thiocarbanolid. A few tenths of a pound of these materials are used with a little pine, or other oil. Some remarkable results have been obtained with their use in dropping pyrite during flotation of chalcopyrite and other sulfides. Many metallic sulfates and other chemicals have been tried. Sheridan has found sodium cyanide to be one of the best "sinkers" for pyrite that we have. The Minerals Separation Co. has developed a "xanthate" that is doing excellent work. (The field is too large to be more than mentioned here.)

Although differential flotation has not given (as a rule) good overall recoveries for each separate mineral in very complex ores, the work so far has given results that are full of promise, and from the viewpoint of immediate realization of profits, a great deal has been accomplished.

### TREATMENT OF ZINC CONCENTRATES

The two principal types of plants treating zinc concentrates (retort and electrolytic) are too well known to require description. As an estimate of their future, the following points will be noted showing the lines along which developments for the treatment of complex ores may take place.

#### *Retort Plants*

Many improvements have been suggested on the technical features of retorting, and work has been done on handling sulfide ores without preroasting. The retort residues containing the unvolatilized metals (with the exception of the zinc) are largely paid at the present time.

The retort itself, although it has a fairly low first cost, is inherently of small capacity and is not well adapted for handling low-grade or complex ores. It requires the labor of strong, hard-working, skillful men—it is becoming increasingly difficult to obtain men of this caliber without paying very high wages. The cost of fuel (*e. g.* natural gas and coal) is rising steadily. The cost of freight haulage from the complex-ore districts to the retort plants, and of the retort residues from the retort plants back to the lead smelters, is high. It is not thought likely, then, that the retort plant will be of any great service in the future to the complex ore field.

#### *Electrolytic-zinc Plants*

The electrolytic plant may be operated very well with the type of labor available at present, although expert technical supervision is essential. From the experience at Trail, B. C., as compared to that at Great Falls, Mont., the admission of a large amount of middling products to the feed will not be looked on with much favor. The recovery is naturally lower with a feed containing a lower amount of zinc, as the iron minerals when present in too large amounts cause the formation of insoluble zinc "ferrites," and high percentages of lead cause fritting in roasting and an excessive amount of wear on the rabble teeth. (The Trail plant is now<sup>1</sup> trying to put its feed into the zinc-concentrate class by the use of selective flotation.) The electrolytic plant has an advantage over the zinc-retort plant in the recovery of the metals after the bulk of the zinc has been removed, and in the relative ease with which the residues may be handled throughout the process. Although the residue

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<sup>1</sup> *Eng. & Min. Jnl.-Pr.* (Sept. 15, 1923) 116, 453.

is somewhat high in zinc after sintering, it is not a bad feed for the lead blast furnace.

As for diluents of the zinc content of concentrates that would not affect its solubility chemically, there would seem little reason why a zinc electrolytic plant could not treat a lower grade feed. It has been shown<sup>6</sup> that as high as 70 per cent. oxidized ores may be successfully treated by leaching by mixing it with 30 per cent. of sulfide concentrates. The soluble silica may be taken care of, and the process made self supporting in acid with some modifications.

An electrolytic plant requires good transportation facilities, cheap power, an ore charge that in the treatment will be self-sustaining in acid, and a neighboring orebody that is large enough to "stand" the high first cost of the plant. (The freight on a 40 per cent. zinc product from Salt Lake City to Joplin is about 1 c. per lb. of zinc.) It is evident that the electrolytic-zinc plant, by strengthening its position behind that of lead, is in a strong place today. The statement has been made<sup>7</sup> that the costs of treatment have been made remarkably low. The purity of the zinc will make it in great demand.

It is difficult, however, to meet all the requirements just noted, especially the treatment-plant sites near the complex-ore fields, where power is available at, say, \$25 per horsepower year. Such combinations of suitable conditions are not many. The present freight rates limit the radius within which a zinc plant may draw its ores, and profitably dispose of its lead residues. The large zinc plant needed for economical operation may exhaust the local ore supply rapidly, or be at intervals crippled by accidental delays in ore delivery. Seemingly, the extension of electrolytic-zinc plants in the Rocky Mountain region is tied up with the development of power sites along the Colorado River or in Idaho, or in the use of "off peak" power, or in steam-power plants in some few localities where fuel is cheap.

The principal losses of the electrolytic-zinc plant are, in order of amount: insoluble zinc left in the residue, mechanical dusting losses during roasting, loss in the cadmium cake, soluble loss in the residue, and the drossing loss in casting. Only the developments that have been made for reducing the first named, and greatest, loss will be considered in the discussion of the sulfating process (p. 484).

#### *Byproducts—Zinc Chloride, etc.*

The production of zinc chloride from oxidized zinc materials by the use of gaseous chlorine has been noted<sup>8</sup> in the technical press. The Great Western Chemical Co. at Pittsburgh, California, is now making

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<sup>6</sup> University of Utah *Research Bull.* (1922-23).

<sup>7</sup> Zinc Inst. *Bull.*, quoting Frederick Laist.

<sup>8</sup> C. G. Maier: *Eng. & Min. Jnl.-Pr.* (Jan. 13, 1923) 115, 51.

zinc chloride from roasted complex ores, and hydrochloric acid made from byproduct chlorine. Although there is not much information at hand, the company appears to be successful and the operation will be limited more by market demands than by any other factor. Should the market develop rapidly for zinc sulfate (for lithopone), or other zinc compounds, the plants using chemical methods for extracting zinc from ores should be able to make them to supply the demand.

### *Processes for Oxidized Basic Ores*

Ammonia is the most promising of all the alkaline reagents that have been suggested for use with oxidized basic ores, and the work of Bretherton<sup>\*</sup> shows that very good results have been obtained. As yet, no commercial plants have been erected; there appear to be technical difficulties that must be solved before ammonia will play the same role for zinc that it does for copper.

### *The Wetherill Grate*

For oxidized zinc ores containing very little lead, the Wetherill grate may be employed for the production of zinc oxide. The market for this product is good, the first cost of the plant is not large, and the type of plant lends itself well to operation in small units. Although mixtures of bituminous coal and coke have been used, anthracite is regarded as the best fuel, but this is not available in many localities. The many physical as well as chemical tests that the marketable product must pass render competent technical supervision imperative.

As an outlet for the complex ores, it is found that the market may be easily oversupplied, when the mixed lead-zinc "oxide" (much of the lead is usually present as the sulfate) field is entered. A study of "Mineral Resources of the United States" will show that although the consumption of lead-zinc oxides in pigments is increasing, the bulk of the zinc is still disposed of in the metallic form.

From the foregoing, then, it would seem that the Wetherill grate process will occupy an important, but limited field as far as the complex ores are concerned.

## REMOVAL OF SMALL AMOUNTS OF LEAD FROM ZINC CONCENTRATES

### *Chloride Processes*

Many schemes have been advanced whereby the separation of lead from zinc in complex minerals might be made by removing the lead instead of the zinc. This reversal of what might be thought the normal method

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<sup>\*</sup> Treatment of Complex Ores by the Ammonia Carbon Dioxide Process. *Trans.* (1914) 46, 802.

is done in order to produce zinc concentrates which are easier to treat, to remove a larger part of the lead (and silver) than would be paid for in the zinc-retort residue, to prepare a zinc concentrate for making a lead-free zinc oxide, or to save freight. Many of these processes have been tried on lead-zinc middling products, which would appear to be a more normal field. Most of these processes make use of the fact that oxidized-lead compounds are soluble in saturated brine solutions. (In order to make some compounds soluble, it is necessary to add an acid to the brine.) If these compounds are not already oxidized, the ores are roasted, as in the Holt-Dern process. If it be desired to treat the raw ore directly, an oxidizing agent (the "ic" salt of a multivalent metal, gaseous chlorine, etc.) is added. Thus Hannay recommends ferric chloride; ferric sulfate has been tried; gaseous chlorine is found to be a powerful oxidizer; and the staff of the Tintic Standard Co. has found the addition of cupric sulfate to the brine solutions to be particularly effective in obtaining a good recovery of the silver. (The use of copper sulfate in the old Russell process is still well remembered.)

Ganelin<sup>10</sup> found that if complex ore from Broken Hill, Australia were heated to about 400° C. in a non-oxidizing atmosphere with zinc chloride, the reaction  $\text{ZnCl}_2 + \text{PbS} = \text{ZnS} + \text{PbCl}_2$  proceeded almost quantitatively, and the silver could be likewise made soluble. The lead and silver chlorides were dissolved in warm brine solution, and precipitated as cement metal by metallic zinc, reforming zinc chloride, which could be reused for treating more ore. N. C. Christensen found the addition of concentrated acid to be effective for some ores tested.

Some of the chloride processes are being vigorously pushed at present, and others are used in commercial operation. Their technical success is largely contingent on the system of precipitation used. Although the electrolytic precipitation of metals from chloride solution has been carried on for many years, practical operating difficulties have caused the users of chloride electrolytes to change to sulfate, whenever possible. Where the foregoing processes leave the blende and pyrite together unaltered and the galena is removed, there is a chance to make a good zinc concentrate by some of the recent flotation methods. The economic factors and the types of ores on which chloride processes have the most opportunity for success have already been noted.

#### *Volatilization as Chlorides*

The relatively small amount of lead usually present in a zinc-sulfide concentrate may be volatilized by heating the charge to about 900° C. Without the addition of salt, lead oxide volatilizes; but the addition of salt insures the more complete removal of the lead as chloride. The

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<sup>10</sup> *Min. Magazine*, London (March, 1920) 22, 181.

degree to which an ore is infusible determines the applicability of this process. The ordinary zinc-sulfide concentrate contains but few fusible substances except lead oxide, lead silicate, and pyrite and these are all present in small amounts. The main field of application of volatilization is the same as that of the other chloride processes mentioned. It has been tried on a semicommercial scale in two plants, but neither of these is operating continuously.

### TREATMENT OF LEAD-ZINC MIDDLING PRODUCTS

Very often good zinc and fairly clean lead products have been made by concentrating, and all the intimately associated minerals that could not be separated have been sent into one product, called the middling product. (The writer has included natural ores of the same nature and approximate composition under the same head.) For years, products of this type have offered to the metallurgist one of his most baffling problems. Some of the leaching schemes used have already been noted.

#### *Concentration after Roasting*

After roasting, the properties of some minerals are changed so that concentrating devices will give much more favorable results. Horwood tried to "flash roast the lead" at low temperature (*e. g.* cover the galena with a thin film of lead sulfate) and to subsequently float the unaltered blende. The process was not a commercial success, largely because of difficulties in regulating the roasting conditions; also, but little was known at that time about flotation. The present methods are mostly based on the idea that the iron minerals unite those of lead and zinc, and that if the nature of the iron mineral be altered, the lead and zinc minerals will adhere to each other much less closely. Thus, if a complex ore is roasted in a Wedge furnace in the regular manner, except that the capacity of the furnace is increased beyond the normal so that the difficultly oxidizable blende will be but little altered, yet much of the pyrite oxidized, often on subsequent tabling much of the galena may be separated as a high-grade product. The difficulty of igniting the blende gives an opportunity to oxidize most of the pyrite and to sulfatize the galena before the blende is altered. If this may be done by establishing furnace conditions that can be readily controlled in commercial operation, a simple practical process would be had, as the unaltered blende could be removed by flotation and the products in the residue would be in a marketable form.

By roasting at low temperature, it has been found possible to magnetize the iron minerals so that they might be removed by electromagnets, or to give the blende and galena such properties that they might be separated electrostatically. As with the Horwood process, the chief difficulty has been with the control of the furnace operation. Flotation to date has



"won out" over these other partly mechanical methods, although it has given poor overall recoveries for each of the various metals.

### *Mixed Lead-zinc Oxides*

The River Smelting Co. has a novel plant at Florence, Colo. The complex ore is roasted and smelted in a reverberatory furnace of the modern type (side charging, and coal-dust firing). Three products are made: Matte, carrying the copper and noble metals; fume containing the lead and zinc; and slag, which is composed of the gangue portions of the ore. The matte is sold as such to the smelters. The fume is caught in a baghouse and subsequently treated on Wetherill grates, recaught, and sold as mixed lead-zinc oxides for pigments. This same general scheme may be utilized with a blast furnace, in place of the reverberatory, by running the former furnace with a hot top. The principal economic difficulty that lies in the operation of a plant of this nature is in the disposal of its lead-zinc oxide, as the market is limited.

### *The Sulfating Process<sup>11</sup>*

It has been noted that the middling product is not a good feed for the electrolytic plants, although doubtless they could work small amounts along with their regular feed. The operators of the sulfating process have found it possible to sulfatize (make water-soluble) a high percentage of the zinc minerals present, even when feeding ores of the middling type into their furnace. This sulfating has been done in a downdraft furnace, using higher hearth temperatures, higher  $\text{SO}_2$  concentration in the gas than is ordinary, and having iron and copper oxides present at such stages that the reaction  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$  would be catalyzed. Enough zinc oxide may be left in the residue to precipitate most of the copper that is made soluble on leaching with water. Except that it contains little colloidal matter, the residue is not greatly different from the present zinc-plant residue, and may be smelted in the same way.

There are but few data for publication on the process, but the "breaking up of ferrites" by  $\text{SO}_2$  (see also the Trail patents and the Great Falls idea of roeroasting the calcine with sulfuric acid) offers a suggestion for the improvement of present practice. If a part of the zinc is to be sold as electrolytic zinc, there will be sulfuric acid to dispose of. Fertilizers and zinc byproducts suggest themselves as possible products for the zinc plant of the future.

### CONCLUSIONS

The present trend in the treatment of complex ores in the Rocky Mountain region is to combine concentration, leaching, and pyrometallurgical methods; to separate the metals at such stages and to use

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<sup>11</sup> *Min. & Met.* (October, 1923) 4, 514.

for each metal the process that economic conditions have shown to be most feasible. The objection will be made that all stage processes obtain for the ultimate recovery of a metal a figure that is the product of a series of recoveries.

Seemingly, if all the metals were carried into solution from the original ore and then followed by a chemical separation like that in the laboratory, or electrolytic precipitation of the metals at different voltages, the best recovery would be obtained. Such a procedure would bring about the elimination of intermediate stages. The successive employment of different solvents may also be considered. Such schemes are not entirely fanciful. For instance, a very cheap supply of nitric acid, such as is now discussed as a possibility for the future, together with improvements in mechanical handling, acid-resisting materials, etc., might make an extremely simple plant flow sheet possible. One stage (roasting before leaching with brine to remove lead) was eliminated in some of the chloride methods given, by having the solution carry its own oxidizer. Recent developments in the oxidization of iron salts would also seem to carry considerable significance along this line.

Although the inadequateness of present methods is clearly recognized, the engineer at a mine is forced always to keep before him the facts that to make money on a given ore, its valuable metals must be extracted by present methods, and that pioneering is slow and costly. This is particularly the case where the metallurgy of complex ores containing several metals must be worked out. The present trend is not to make radical departures from accepted practice, but to improve each of the stages now used in the treatment of the simpler ores, and to combine effectively these improvements to meet the new conditions imposed by the introduction of several metals. For the benefit of the future metallurgist, it may be a timely suggestion that the values which are not saved should be impounded and left in as simple a form as possible; for instance, as a product like that of the original ore, rather than in a slag, or a speiss.

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## Electrolytic Zinc from Complex Ores

BY U. C. TAINTON AND L. T. LEYSON, KELLOGG, IDA.

(New York Meeting, February, 1924)

SOME time ago, at a meeting of the Institute Prof. J. W. Richards<sup>1</sup> said, "I take exception to the statement that all the factors in the production of electrolytic zinc were known long ago. . . . There is possible in my opinion an improvement of perhaps 50 per cent. in the new electrolytic processes." An examination of the literature of the subject will show the justness of Professor Richards' contention. The work of the earlier investigators was carried on in the shadow of difficulties that, today, are hardly more than memories. We seldom hear now of zinc sponge, that *bête noir* of the electrolytic-zinc pioneers.

Zinc sponge was the name given to a peculiar, soft, black, non-adherent form of zinc deposit that was utterly useless for melting into ingot form. At the big plant at Cockle Creek, New South Wales, in 1897, Edgar Ashcroft<sup>2</sup> said that the solution in the plant would suddenly, and without ascertainable cause, go "bad" and begin to deposit spongy zinc. The most delicate, even spectroscopic, methods of analysis were unable to detect any difference between "good" solution and "bad" solution; either form might change to the other on being kept for a while. When it is added that an outbreak of this insidious disease (which appeared to be infectious, or at least contagious) could be dealt with only by discarding the solution and washing out all tanks and pipe lines, some idea may be gathered of the troubles of the zinc electrometallurgist in what may be spoken of as the "sponge age" of electrolytic zinc.

Thanks to the efforts of a number of investigators, we are today able to diagnose with considerable certitude the nature of the malady that puzzled Ashcroft and his co-workers. The researches of Mylius and

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<sup>1</sup> R. G. Hall: Some Economic Factors in the Production of Electrolytic Zinc. *Trans.* (1917) 57, 718.

<sup>2</sup> Edgar A. Ashcroft: The Treatment of Broken Hill Sulphide Ores by Wet Extraction Process and the Electrolytic Deposition of Zinc. *Trans. Inst. of Min. & Met.* (1897) 6, 232.

Fromm<sup>3</sup> showed the close relationship between spongy zinc and basic salts in the electrolyte and drew attention to the necessity of keeping the electrolyte slightly acid. They also noted the extraordinary effect of minute quantities of impurities, such as arsenic, in bringing about spongy zinc. The development of the theory of overvoltage supplied the link that connected these two apparently unrelated facts. A little later, the work of Hantsch<sup>4</sup> and others, in showing the existence of colloidal zinc hydrate in basic solutions, and the theory of Muller and Bahntje,<sup>5</sup> with reference to the action of colloids in electrolysis, gave additional information on the cause and cure of the zinc-sponge evil.

The electrolytic-zinc battle, however, was by no means won; the greatest difficulty was with the anode and its decomposition products. The seriousness of this trouble may be gaged by the fact that even platinum anodes were tried, and rejected because platinum dissolved in the organic acids always present in the electrolyte. Fused magnetite anodes suffered from the same defect, carbon anodes disintegrated, lead fouled the electrolyte. Ferchland<sup>6</sup> and Siemens Halske<sup>7</sup> expended much ingenuity and effort on the problem, with the anode of pure precipitated manganese dioxide as the result. It is only comparatively recently that the use of lead anodes has been successful; the reason for this, it appears,<sup>8</sup> resides in the higher current densities now employed.

No sooner had some measure of control over the conditions of electrolysis been acquired than another difficulty presented itself; this was the fouling of the solution by the accumulation of impurities. It appears, from the literature, that manganese was one of the most troublesome of these intruders; Edgar Ashcroft said:

"The accumulation of manganese salts is considerable and has so far prevented true cyclic working."

Manganese, of course, is almost universally present in zinc ores; and even were it not, the necessity for oxidizing the iron in the leach (for which purpose a manganese compound was usually employed) led to its presence in the electrolyte. Laszczynski,<sup>9</sup> who for some years operated an electrolytic-zinc plant in Silesia, stated: "Since the iron must be removed from the liquor before zinc is electrodeposited and a permanganate is the best oxidant for completing the conversion of ferrous salts into the ferric state prior to precipitation as hydrate, the liquor always contains manganous salts which must not be allowed to pass into the

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<sup>3</sup> Mylius and Fromm: *Zeit. f. anorgan. Chem.* (1895) 9, 164.

<sup>4</sup> Hantsch: *Zeit. f. anorgan. Chem.* (1902) 30, 298.

<sup>5</sup> Muller and Bahntje: *Zeit. f. Elektrochem.* (1906) 12, 317.

<sup>6</sup> Brit. Pat. 24806 (1906).

<sup>7</sup> Brit. Pat. 15128 (1911).

<sup>8</sup> Tainton: *Trans. Am. Electrochem. Soc.* (1922) 41.

<sup>9</sup> Wintle: Brit. Pat. 1341 (1910).

higher states of oxidation, a result which is inevitable in the ordinary method of electrodepositing zinc."

Manganese, of course, is no longer regarded as a cumulative impurity, and in some respects is regarded as beneficial. It is not easy to say exactly how the change has come about. The writer believes that, like the use of lead anodes, the improvement is probably the result of using higher current densities. At least this is the only certain difference between standard modern electrolytic conditions and those of Siemens Halske 15 years ago.

The problem of impurities in the electrolyte, which even now calls for constant vigilance from the zinc-plant manager, stood for many years. As a solution derived from the acid leaching of a zinc ore might contain practically every element in the chemical calendar, it was feared that the necessary purification processes would become too complex and costly to be commercially practicable. Some of the earlier investigators went rather too far in setting their standards, thereby handicapping themselves unnecessarily. For example, Siemens Halske demanded that "every other metal (but zinc) and even carbon, should be completely excluded," an ideal that in practice is quite beyond realization.

With further experience, however, it was found that certain impurities were much less harmful than others and gradually through the continued efforts of many different workers (Ferchland, Borchers,<sup>10</sup> Cowper Coles,<sup>11</sup> Hoepfner,<sup>12</sup> Laszczynski,<sup>13</sup> Engelhardt and Huth<sup>14</sup> among others) there was evolved the flow sheet of a system that would prevent accumulation of impurities. Iron was oxidized and precipitated, together with most of the arsenic and antimony, in the pulp before filtration. From the filtered solution, the remaining metals electronegative to zinc were removed by precipitation with zinc dust. This system, if properly worked, took care of all interfering impurities except a small group (nickel, cobalt, vanadium, etc.) which, if present in any considerable quantity, may have to be made the subject of special purification methods.

Even today, this field is by no means fully explored. It is understood, of course, that the accumulation of impurities no longer prevents the true cyclic working of the electrolytic-zinc process. It is, however, impossible commercially to prepare solution not containing some trace of impurity—the methods of removal are never absolutely complete—

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<sup>10</sup> Borchers: *Zeit. f. Elektrochem.* (1895) 2.

<sup>11</sup> U. S. Pat. 672637 (1901).

<sup>12</sup> Hoepfner: *Eng. & Min. Jnl.* (1903) 75.

<sup>13</sup> Laszczynski: *Zeit. f. Elektrochem.* (1909) 15, 456.

<sup>14</sup> U. S. Pat. 935250 (1909).

and the matter becomes one of striking an economic balance between a lowered current efficiency, caused by small amounts of impurities, and the cost of their removal from the solution. How important this problem is may be seen from the following quotation<sup>18</sup> from the most recent and authoritative description of present-day practice: "When the problem of producing an electrolyte of absolute purity has been solved, the design of electrolytic-zinc plants and the operating conditions of the electrolyzing division will be greatly changed from the present trend. Where 75 per cent. ampere efficiency is now considered good practice, 85 to 90 per cent. is easily obtainable with slightly more pure solutions." On account of the fact that the current efficiency obtainable from an impure electrolyte rapidly falls as deposits become thicker, one of the large zinc plants has recently found it of advantage to reduce its deposition period from 48 hr. to 24. Although the deposits so obtained are very thin, weighing only about  $1\frac{1}{2}$  lb. per sq. ft., the increased current efficiency more than offsets the extra cost of stripping the zinc.

While, in the foregoing, attention has been directed particularly toward the troubles encountered in the actual electrolysis, it must not be supposed that the roasting and lixiviation of the ore has been free from difficulty. It would take too long to detail the many obstacles that have been met and overcome. Two serious difficulties have not yet been fully overcome. These may be epitomized under the names of zinc ferrite and gelatinous silica.

#### PERCENTAGE OF ZINC EXTRACTION

The fundamental reactions involved in the leaching of zinc ores give, at first sight, every promise of possible completeness. Zinc sulfide may be completely oxidized without difficulty. Zinc oxide is totally soluble in sulfuric acid, even in hot zinc-sulfate solution. May we not expect, therefore, to obtain by acid leaching a zinc extraction approximating 100 per cent.? So, doubtless, reasoned the first workers in zinc hydrometallurgy. But practice soon indicated the existence of an error in the argument. There appeared unaccountable difficulties in dissolving the zinc and further difficulties in separating the solution from the residue. Investigation proved that, during the roast, ferric oxide and zinc oxide combined to some extent to form zinc ferrite,  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ , insoluble in dilute acids. Furthermore, when a roasted zinc ore is treated with acid, a certain quantity of iron and silica pass into solution. When the acid is later neutralized by continued addition of roasted ore, the iron and silica are precipitated, in the form of hydrated ferric oxide and gelatinous

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<sup>18</sup> Laist, Frick, Elton and Caples: Electrolytic Zinc Plant of Anaconda Copper Mining Co. *Trans.* (1920) 64, 699.

silica, respectively. These two substances, at the best, tend to reduce filtration speeds; and, at the worst, may make the separation of the solution from the ore an utter impossibility.

As a result of these phenomena, the residues from the modern electrolytic-zinc plant carry usually from 12 to 20 per cent. of zinc, the average at the present day being closer to the higher than to the lower figure. Ralston<sup>16</sup> says: "Recoveries of zinc in hydrometallurgical practice have thus far (1921) averaged only about 70 per cent." Experience at one of the large plants has been crystallized into a formula that the percentage extraction of zinc which can be expected from a given low-grade concentrate (25-35 per cent. Zn) may be predicted with considerable approach to accuracy by multiplying the percentage of zinc present by two (Blaylock). That is to say, a 34 per cent. zinc concentrate yields about 68 per cent. recovery, and so on. This empirical rule does not apply to concentrates carrying more than 35 per cent. of zinc, for which extractions are usually lower than it would indicate.

#### FLOW SHEETS OF ELECTROLYTIC-ZINC PLANTS

The increasing complexity of the flow sheet of the modern electrolytic-zinc plant shows the importance of the considerations mentioned; namely, the necessity of a pure solution on the one hand, and the difficulty of reconciling this condition with that of a high extraction of zinc. It is evident that these requirements are, to some extent, antagonistic; for if the residue going out of the plant has been treated with a solvent sufficiently active to make a high extraction of the zinc values, other constituents of the ore must also have been taken into solution and must be eliminated before the solution can be used for electrolysis.

A double leaching treatment, as recommended by Isherwood,<sup>17</sup> Stewart<sup>18</sup> and others, and practiced at Trail and Great Falls, is one method of dealing with this difficulty. The residues going out of the plant are finished in acid solution, but this solution is separated and neutralized with an excess of roasted ore, many other constituents of the solution being thus precipitated. This basic solution is then separated and goes forward to precipitation, while the solids, containing an excess of calcine, are treated with the acid solution before going out of the plant.

The ideal theoretical case of this method would be a counter-current system wherein the roasted ore dropped through a pipe against an ascend-

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<sup>16</sup> Oliver C. Ralston: "Electrodeposition and Hydrometallurgy of Zinc." McGraw Hill Book Co., New York, 1921.

<sup>17</sup> Brit. Pat. 22855 (1912).

<sup>18</sup> U. S. Pat. 1320805 (1919).

ing current of acid solution.<sup>19</sup> The residues going out at the bottom of the column would thus be finished in acid solution, whereas the solution leaving at the top would be thoroughly neutralized with an excess of calcine—a condition favorable to the precipitation of many objectionable constituents.

A moment's consideration of this case, however, makes it clear that the acid entering at the bottom of the pipe must not be strong enough to redissolve these precipitated impurities. Considering the case of zinc

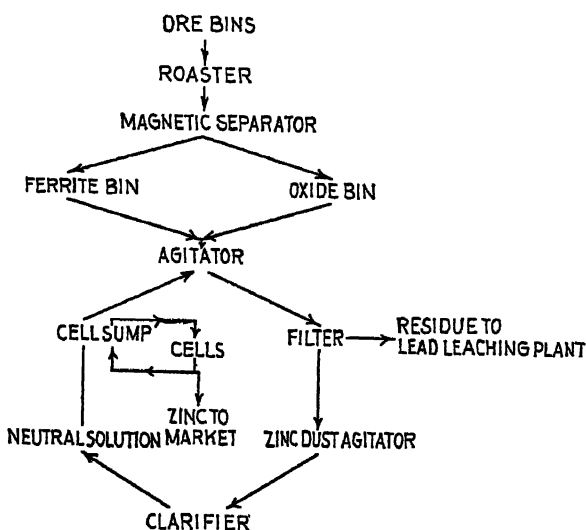


FIG. 1.—HIGH-ACID PROCESS FLOW SHEET.

ferrite, for example, if the acid entering from below were strong enough to dissolve this compound, the dissolved iron would be precipitated at the top of the pipe and would then descend, to be again dissolved, together with more iron from the new ore. Iron would thus rapidly accumulate and the process would cease.

The double-treatment system, therefore, while effective in extracting zinc oxide cannot be employed to break up zinc ferrite. The manager of the zinc plant has, therefore, centered his effort on obtaining as much as possible of the zinc in oxide form. The most effective way of doing this is to keep iron out of the zinc concentrate, which method has been generally adopted. Through the purchase of high-grade concentrate and the use of selective methods of concentration, the electrolytic-zinc plants have steadily raised the grade of their plant feed, until their requirements are

<sup>19</sup> Gillies: U. S. Pat. 875424 (1906).



almost as exacting as those of the zinc smelter. The most recent ore-purchasing schedules of the Great Falls and Trail plants are good examples of this fact. These requirements have tended to change the status of electrolytic zinc from what was at first hoped for—a general solution of the complex-ore problem—to that of a process alternative to, and competitive with, the old smelting method.

Some years ago, there were published<sup>20</sup> certain apparently anomalous results in connection with zinc electrolysis. It was found that if the cathodic current density and the free acid in the electrolyte were simultaneously raised to very high values, particularly in the presence of a small quantity of colloidal matter, the efficiency curve started to rise and zinc deposits of exceptionally good quality could be obtained even from solutions containing considerable quantities of impurity. These phenomena were somewhat at variance with the ideas then current regarding the limitations of zinc electrolysis. At the same time, it was recognized that they might prove of practical value. For example, Dr. O. P. Watts<sup>21</sup> said: "Doctor Pring's experiments disclose new and undreamed-of possibilities in the electrometallurgy of zinc and emphasize the importance of trying experiments which, in the light of our present imperfect knowledge of the laws of nature and the properties of matter, would seem sure to fail."

It was indeed evident that if these conditions could be applied in practice, certain advantages would follow. For example, the use of a return electrolyte carrying, say, 28 per cent. free acid instead of 7 per cent. would reduce to one quarter the quantity of solution to be neutralized, filtered, purified, etc., for a given output of zinc. Similarly, the use of a current density of 100 amp. per sq. ft. would necessitate the use of only one quarter the electrode area, cell capacity, etc. Also the possibility of using less pure solutions would minimize one of the main difficulties in connection with the continuous production of good zinc deposits and the maintenance of a high current efficiency.

The practical application of these ideas to the electrolytic recovery of zinc from ores was therefore undertaken by the Rand Mines Ltd., of South Africa. The company was assisted in this enterprise by Charles Butters, of Oakland, Calif. As was to be expected, many difficulties were encountered at first, more especially on the engineering side.

The mechanical equipment previously used in zinc leaching, filtration, and electrolysis proved inadequate to handle the special problems that the conditions of strong acids and high current densities present. Indeed, the application of these conditions to the standard machinery of electrolytic-zinc practice was early recognized to be entirely out of the question. It was necessary to devise special methods and apparatus, without which the commercial operation of the process on many ores

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<sup>20</sup> Pring and Tainton: *Jnl. Chem. Soc.* (1914) 105, I, 710.

<sup>21</sup> O. P. Watts: *Trans. Am. Electrochem. Soc.* (1914) 25, 295.

would be almost impracticable and without a knowledge of which any tests under these conditions would almost certainly fail. Some of these methods are published here for the first time.

### EXPERIMENTAL PLANT

To insure that all engineering difficulties were completely worked out, it was considered advisable to erect a pilot plant having a capacity of 15 tons of concentrate per day, and operate it continuously. This plant was erected at Martinez, Calif., each unit in it, roasting, filtration, etc., being of full commercial size, so that any desired capacity might be obtained by simply multiplying units.

Operation was continued until all units of the plant had been thoroughly tested and found to stand up to continuous service. This involved considerable experimental work, followed by 8 months continuous operation, in 1920, during which 1600 tons of zinc concentrate were run through the plant. These results were extended by 6 months operation of a test plant at the Bunker Hill & Sullivan Mining & Concentrating Co., at Kellogg, Ida. In certain departments, notably filters, acid pumps, and electrolytic cells, several types were tried before satisfactory operation could be secured. However, as the mechanical operation was stabilized, it became apparent that the conditions in question (strong acids and high current densities) lent themselves easily and naturally to methods of dealing with the two big problems previously mentioned—those of zinc ferrite and gelatinous silica—while still maintaining the simplest type of flow sheet. It has proved practicable to make good commercial recoveries (about 90 per cent.) from ores in which only 75 per cent. of the zinc was “soluble.” It is also possible to leach and filter oxidized zinc ores, which, as is well known, usually give rise to so much gelatinous silica as to render their direct hydrometallurgical treatment infeasible.

These results arise quite automatically, so to speak, from the use of high acid concentrations. The feature of our work that has attracted most attention has been the high current density used in electrolysis; but this is subsidiary, though necessary, to the use of strong acid leaching solutions. The development of our practice has been marked by a steady increase in the acid strength of the electrolyte, leading to higher extractions, better zinc deposits, and lower power consumptions. At the outset, we did not dare go beyond 20 per cent. acid. With increasing acid strength, however, the plant results consistently improved until now the return electrolyte carries usually about 28 per cent. of free acid, and occasionally exceeds 30 per cent. This is about as high as it is possible to go using neutral solutions that are stable (*i. e.* do not crystallize) at room temperatures.

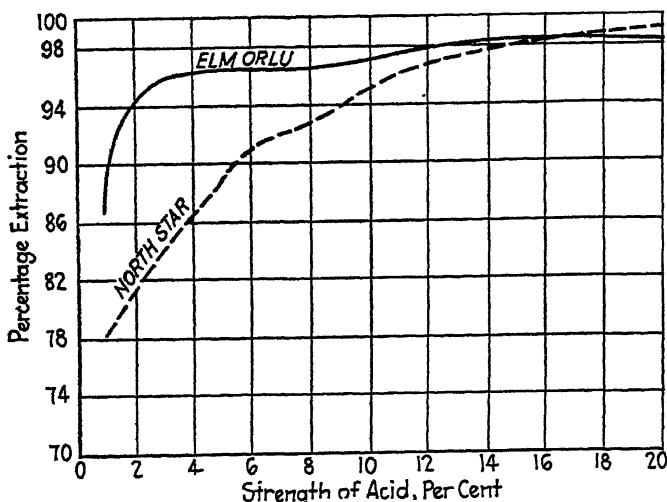


FIG. 2.—PER CENT. ZINC SOLUBLE IN SULFURIC ACID OF VARYING STRENGTH AT 100° C. AND 1 HR. CONTACT; ROASTED CONCENTRATE FROM ELM ORLU MINE, BUTTE, AND NORTH STAR MINE, HAILEY, IDAHO.

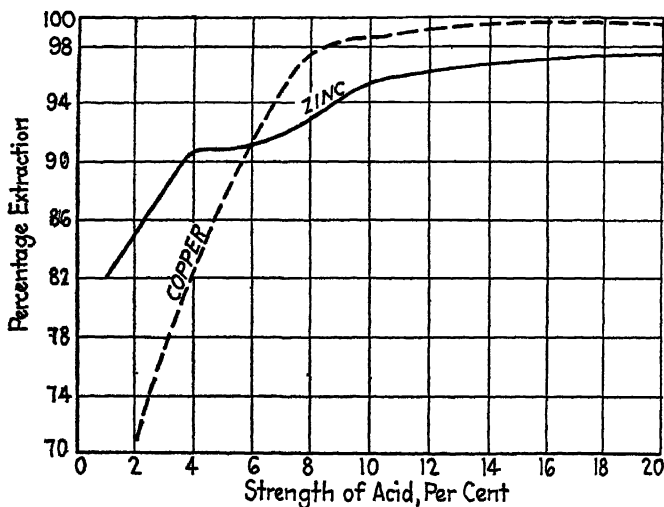


FIG. 3.—PER CENT. ZINC AND COPPER SOLUBLE IN SULFURIC ACID, AT 100° C. AND 1 HR. CONTACT; ROASTED CONCENTRATE FROM AFTERTHOUGHT MINE, SHASTA CO., CALIF.

NOTE.—The expression per cent. of acid, as used here, represents ordinary plant usage and is not a true percentage. What is meant by  $x$  per cent. of acid is  $x$  grams of acid per 100 c. c. of solution, or 10 $x$  gm. acid per liter of solution; thus 28 per cent. acid represents 280 gm. per liter  $H_2SO_4$ .

As would be expected, the quantity of zinc extracted from an ore is greater, the stronger the acid used for leaching. To show the behavior of any given ore in this respect, 1-gm. samples are treated for a fixed time (1 hr.) at fixed temperature (100° C.) with an excess (150 c. c.) of acid of various strengths. The mixtures are filtered and zinc determined both in the solution and in the residue. The percentage extraction is plotted against acid strength. A few representative curves, Figs. 2 to 5, are shown for calcines of the following composition:

	PER CENT. ZINC	PER CENT. COPPER	PER CENT. LEAD	PER CENT. IRON	PER CENT. INSOLUBLE
Afterthought, Shasta, Calif...	24.7	4.74	0.5	15.1	
North Star, Hailey, Ida.....	37.0		8.7	13.2	9.4
Elm Orlu, Butte, Mont.....	59.8		3.05	4.3	11.0
Star, Mullan, Ida.....	41.1	0.15	15.9	9.4	5.1

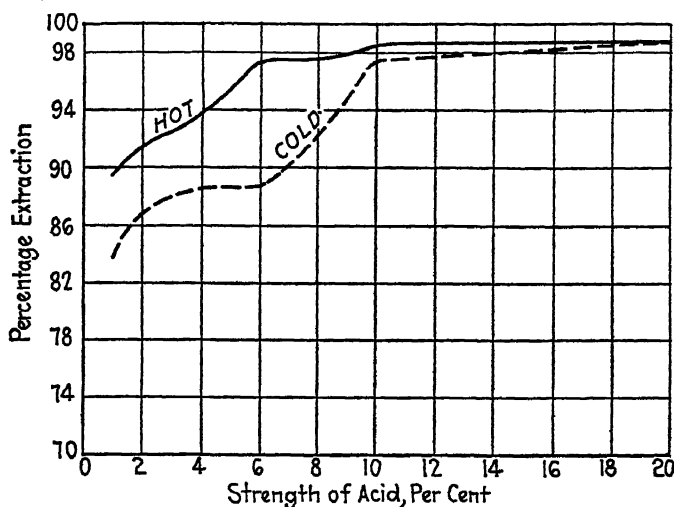


FIG. 4.—PER CENT. ZINC SOLUBLE IN ACID OF VARYING STRENGTH AT 100° C. AND ROOM TEMPERATURE, CONCENTRATE FROM STAR MINE, MULLAN, IDAHO.

TABLE 1.—Percentage of Total Zinc Extracted

Strength Acid, Per Cent.	North Star	Afterthought		Elm Orlu	Star Idaho	
		Zinc	Copper		Hot	Cold
1	78.2	81.7		86.4	89.5	83.5
2	81.4	85.0	70.6	94.4	91.5	86.8
4	86.3	90.6		96.1	93.75	88.5
6	91.2	91.2		96.3	97.5	89.0
8	92.6	92.8	97.4	96.0	97.5	92.25
10	95.3	95.5	98.4	97.3	98.6	97.4
15	98.0	96.8	99.9	98.3	98.4	
20	99.4	97.3	99.9	98.5	98.7	98.6

The extractions are shown in Table 1. For the sake of comparison, the extractions for the Star ore are shown at both 100° C. and room temperature, Fig. 4.

#### EFFECT OF ZINC FERRITE ON EXTRACTION

To determine what part the zinc ferrite plays in the extraction, a sample of an ore was finely pulverized and leached with a hot strong (20 per cent.) solution of ammoniacal-ammonium chloride until the filtrate no longer gave a test for zinc; in this way all the zinc oxide and

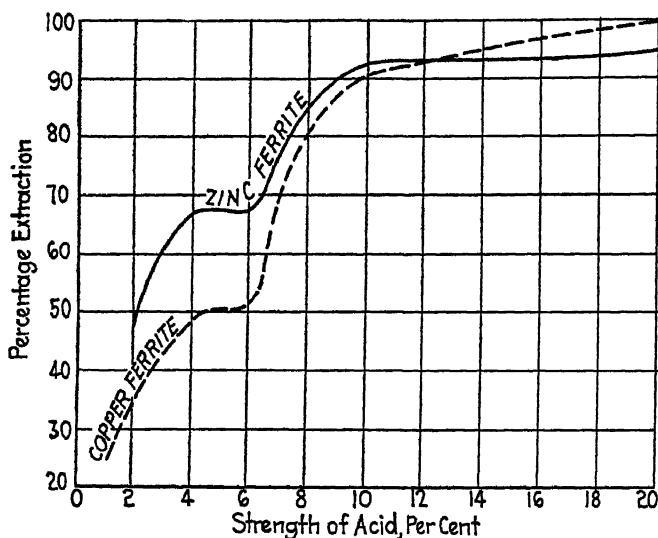


FIG. 5.—SOLUBILITY OF ZINC AND COPPER FERRITES IN VARYING STRENGTHS OF ACID AT 100° C; ROASTED AFTERTHOUGHT CONCENTRATE FROM WHICH ALL SOLUBLE ZINC AND COPPER HAS BEEN REMOVED BY LEACHING WITH AMMONIACAL AMMONIUM-CHLORIDE SOLUTION

zinc sulfate were completely removed. The residue containing the zinc ferrite, together with some silicate, unroasted sulfide, etc., was leached with different strengths of acid, as before. The results, shown in Fig. 5, are as follows:

	BEFORE LEACHING WITH $\text{NH}_4\text{Cl}$ , PER CENT.	RESIDUE AFTER LEACH- ING 56.4 PER CENT. OF ORIGINAL WEIGHT, PER CENT.
Zinc.....	22.7	15.8
Copper.....	5.03	3.85
Iron.....	17.0	30.1

## EFFECT OF DIFFERENT STRENGTHS OF ACID

The effect on this residue of different strengths of acid was as follows:

PER CENT. H <sub>2</sub> SO <sub>4</sub>	ZINC EXTRACTION, PER CENT.	COPPER EXTRACTION, PER CENT.	PER CENT. H <sub>2</sub> SO <sub>4</sub>	ZINC EXTRACTION, PER CENT.	COPPER EXTRACTION, PER CENT.
2	47.0	23.9	10	93.1	91.0
4	67.1	48.8	15	93.1	97.0
6	67.2	52.2	20	94.5	99.4
8	85.0	80.6			

The curve, Fig. 5, exhibits, in an exaggerated degree, the characteristics of the other curves; namely, the slowing up of extractions between 4 and 8 per cent. acid, then a rapid rise until 10 per cent. and a gradual increase up to 20 per cent. acid.

Because the curve, Fig. 2, shows an extraction of about 91 per cent. on North Star ore with 6 per cent. acid, it must not be assumed that any

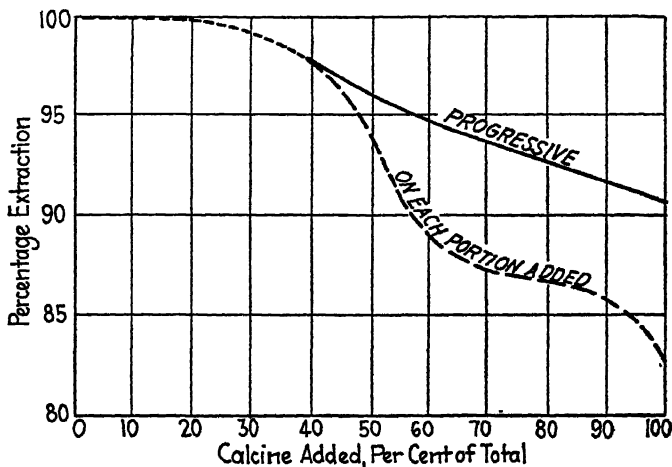


FIG. 6.—EXTRACTION OF ZINC OBTAINED IN PLANT LEACH DURING NEUTRALIZATION OF 27.5 PER CENT. ACID (HOT) WITH ROASTED STAR CONCENTRATE; ILLUSTRATING FALLING OFF IN EXTRACTION AS STRENGTH OF ACID IS REDUCED.

such extraction could be obtained in a plant when using return electrolyte carrying 6 per cent. of free acid. In the first place, these figures are obtained by keeping for 1 hr. at boiling temperatures, whereas ordinarily plant solutions are used cold, and ore is added rapidly. Again, a large excess of acid was used in these tests, so that the whole of the sample is treated with acid of that strength. In the case of neutralization of return electrolyte in the zinc plant, it is necessary to deal with a continually falling acid strength, eventually reaching neutrality, so that the average acid strength is only one-half that of the return electrolyte. For these reasons, the plant extraction that can be expected with 6 per cent.

free acid in the electrolyte is usually about that shown on the curves for the 1 per cent. acid strength. On the other hand if, say, 30 per cent. of free acid is used, the extraction will be greatly increased. In the first place, the heat of the reaction (solution of  $\text{ZnO}$ ) is sufficient to raise the temperature considerably; second, two-thirds of the acid range lies above 10 per cent. which, as the curves show, is sufficient to dissolve nearly all the more insoluble zinc compounds.

To determine how this extraction varies in practice, samples were drawn from a tank during the progress of neutralization of a charge of return electrolyte carrying initially 27.5 per cent. of free acid. The different pulp samples were filtered, washed, the filtrate analyzed for iron and the solids for zinc. The results, shown in Fig. 6, are as follows:

PER CENT. ADDED TOTAL CALCINE	IRON, GRAMS PER LITER IN SOLUTION	ZINC IN RESIDUE, PER CENT.	TOTAL PROGRES- SIVE EXTRACTION OF ZINC, PER CENT.	EXTRACTION AT EACH POINT, PER CENT.
40	22.1	2.0	97.6	97.6
60	18.5	4.0	94.8	89.2
80	4.2	5.5	92.8	86.8
100	0.06	6.65	90.9	83.3

The fourth column represents the total progressive extraction on all calcine added up to that point. The fifth column is the extraction for the portion added since the last sample was taken. For example, the average extraction on the whole charge is 90.9 per cent. of the zinc; the average extraction on the first 40 per cent. of calcine added is 97.6 per cent., and on the last 20 per cent. only 83.3 per cent.

The falling off in the extraction in the lower acid ranges is very striking. Unless acid strength exceeds 10 per cent., it is almost hopeless to expect to dissolve anything but zinc sulfate or zinc oxide; all zinc ferrite put in below this point is lost. This fact is recognized at plants where low-acid leaching is employed. It is mainly for this reason that the progress in electrolytic-zinc practice has been marked by the continual attempt to reduce the iron-zinc ratio in the plant feed.

#### MAGNETIC SEPARATION OF ZINC FERRITE

It was thought that if the zinc ferrite in the calcine could be separated from the zinc oxide, it would be possible to add the ferrite first to a strongly acid solution (say, 28 per cent.) until the acid strength was somewhat reduced, and then complete the neutralization with the zinc oxide portion free from ferrite, and so obtain a still higher extraction. Investigation showed that such a separation could be easily accomplished magnetically.

Below are shown extraction figures obtained by leaching a certain concentrate (Afterthought, Calif.) with increasing strengths of acid; this same ore was then separated magnetically into two portions approxi-

mately equal in amount, and the extraction curve obtained for the two portions:

	ZINC, PER CENT.	COPPER, PER CENT.
Original.....	24.7	4.74
Magnetic portion, 34 per cent. of total.....	12.5	7.6
Non-magnetic portion, 66 per cent. of total.....	31.2	3.25

STRENGTH OF ACID, PER CENT.	ORIGINAL		EXTRACTION		OXIDE PORTION	
	ZINC, PER CENT.	COPPER, PER CENT.	FERRITE PORTION ZINC, PER CENT.	COPPER, PER CENT.	ZINC, PER CENT.	COPPER, PER CENT.
2	85.0	70.6	62.1	58.3	96.5	71.1
10	95.5	98.4	90.0	97.5	98.0	99.1
20	97.3	99.9	95.2	99.9	98.3	99.9

The zinc-oxide portion shows very little difference with increasing acid strength, but the increase is considerable in the case of the magnetic (ferrite) portion. Evidently, if the ferrite is not allowed to come into contact with acid below 10 per cent. strength, a high extraction will be obtained.

The introduction of a magnetic separator (of the simple deflecting-pulley type, Fig. 7) into the plant flow sheet immediately confirmed the theoretical predictions. For example, on the Afterthought concentrate

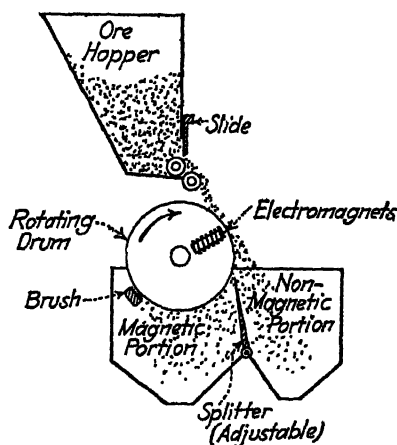


FIG. 7.—TYPE OF MAGNETIC SEPARATOR USED FOR SEPARATION OF ZINC FERRITE FROM ZINC OXIDE IN ROASTED ZINC CONCENTRATE.

(22 per cent. zinc, 5 per cent. copper) the extraction of copper was raised from 60 to 85 per cent. and that of zinc from 85 to 91 per cent. The amount of copper ordinarily extracted at electrolytic-zinc plants is about 20 per cent. (Hansen<sup>22</sup>). On a Canadian zinc concentrate (43 per cent. zinc, 7 per cent. iron), the average extraction of the zinc during two months operation was 94.1 per cent., and of the 5.9 per cent. left in

<sup>22</sup> Electrolytic Zinc. *Trans.* (1920) 64, 85.



residue, 4.6 per cent. was in the form of sulfide, because of poor roasting. The extraction of available zinc was, therefore, in excess of 98 per cent. The residues usually carry from 4 to 8 per cent. zinc, corresponding to a range of grade of the calcine from 25 to 50 per cent.

With this method it is not necessary to obtain a sharp separation of the zinc oxide and zinc ferrite. Ordinarily, the quantity of zinc as ferrite is comparatively small compared with that as oxide. For example, in the case of a calcine carrying 30 per cent. zinc and 15 per cent. iron, assuming all the iron present to be combined with the zinc ferrite,  $\text{ZnOFe}_2\text{O}_3$ , the maximum zinc so combined is 29 per cent. of the total zinc. As ferrite dissolves fairly readily in acid of more than 10 per cent. strength, and as our return electrolyte carries about 28 per cent. of free acid, all that is required is a rough separation, say into two equal parts, one part containing all the ferrite zinc (say 29 per cent. of the total zinc present) together with 21 per cent. of zinc other than ferrite, and the other part containing the remaining 50 per cent. of the total zinc in the form of oxide.

If the magnetic portion is added first to the 28 per cent. acid in sufficient quantity to consume one-half the acid, all of the ferrite will receive thorough treatment. The remaining half of the acid may then be neutralized with the non-magnetic portion. Evidently all that is to be sought is to keep ferrite, as much as possible, out of the oxide portion; the presence of oxide in the ferrite is unobjectionable. This allows a very simple type of magnetic separator.

#### ADVANTAGE OF DISSOLVING ZINC IN FERRITE FORM

An advantage accruing from the ability to dissolve zinc in ferrite form is that so close a control on the roasting is not necessary. Because of the formation of ferrite and the large quantity of zinc sulfate left in the filter cakes, the large electrolytic-zinc plants decided to change from an oxidizing to a sulfating roast; *i. e.*, a slow roast at a low temperature. This, however, has its disadvantages. Laist<sup>22</sup> says "More time is required for sulfate roasting, which means that the capacity will be less and the fuel consumption greater. The gas volume is greater when sulfate roasting so that more flue dust is produced." Where, however, the formation of ferrites is unobjectionable, higher temperatures can be used and greater capacity obtained. The roaster installation for any given output of zinc can thus be correspondingly reduced.

It will be noticed, in the curve (Fig. 6) for progressive extraction during the neutralization of the return electrolyte, that the quantity of iron dissolved with an initial acid strength of 27.5 per cent. reaches 22.1 gm. per liter; this compares with 0.75 gm. per liter dissolved when using

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<sup>22</sup> *Trans.* (1920) 64, 710.

6 per cent. acid.<sup>24</sup> About thirty times as much ferric hydrate per unit volume of solution is thus precipitated in the pulp before the end of the neutralization. This precipitated ferric hydrate represents the means on which the zinc plant relies for the elimination of its arsenic and antimony, which are the two impurities most to be feared in ordinary zinc electrolysis. Laist says "Antimony and arsenic are particularly injurious, causing very poor current efficiency when present in amounts so small as almost to defy detection." Laist and Elton<sup>25</sup> have patented the addition of scrap iron to the acid sump or iron salts to the solution in order to offset this difficulty. C. A. Hansen<sup>26</sup> says: "The trouble in the leaching plant has been due to leaching too little iron rather than too much. At Bully Hill, when it was found that dissolved iron was essential to the complete removal of arsenic and antimony, we tried to roast the ore so that more iron would dissolve; to use such acid concentrations as would lead to dissolving more iron; and finally purchased iron and iron salts as being the cheaper alternative."

It has been clearly shown (Biltz)<sup>27</sup> that the removal of arsenic from solution by means of ferric hydrate is not a true chemical reaction but an adsorption phenomenon expressed by the ordinary adsorption equation  $E = BA^P$ , where  $E$  is the concentration of adsorbed substance in the adsorbing phase,  $A$  is the concentration of adsorbed substance in solution at equilibrium and  $B$  and  $P$  are constants. Typical values for the two constants in this case are  $B = 170$  and  $P = 0.195$ . The final concentration of arsenic in solution will therefore decrease very rapidly as the quantity of iron is increased—approximately inversely as the fifth power.<sup>28</sup> That is to say, for any given case doubling the quantity of ferric hydrate will reduce the residual arsenic left in solution to about  $\frac{1}{32}$ ; by using four times as much ferric hydrate, the residual arsenic concentration will be about  $\frac{1}{512}$ ; and so on. Using thirty times as much ferric hydrate, the ultimate arsenic concentration would be of the order of one twenty four millionth.

It is clear, therefore, that the solutions obtained from the strong acid leach will be, for all intents and purposes, free from arsenic and antimony no matter what amounts of these elements are present in the ore. For the sake of experiment, we have charged into the plant agitators as much as 10 per cent. of arsenic-bearing flue dust (8.5 per cent. As) with the regular calcine without detecting any arsenic in the solution. Normally, after roasting, the amount of arsenic and antimony in the

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<sup>24</sup> Laist *et al.*: *Op. cit.*, 717.

<sup>25</sup> U. S. Pat. 1255436 (1918).

<sup>26</sup> *Loc. cit.*

<sup>27</sup> *Ber. Deut. Chem. Gesell.* (1904) **37**, III, 3138.

<sup>28</sup> Maitland C. Boswell and J. V. Dickson: *Jnl. Am. Chem. Soc.* (1918) **40**, 1793-1801.

calcine is relatively small; using strong acid leach conditions, the arsenic-antimony problem may be finally dismissed.

It might be expected that the presence of so much ferric hydrate in the pulp would lead to filtration difficulties. There exists, however, a rather remarkable compensatory effect. C. A. Hansen<sup>29</sup> thus expresses the result, "High acid concentrations bring about high leaching-tank temperatures and high leaching-tank temperatures conduce to excellent coagulation of the colloidal solids and so make filtration possible." Laist<sup>30</sup> also says "Too low an acid for a long period results in low recovery due to undissolved ZnO and to high moisture in the filter cake caused by precipitating ferric hydroxide, gelatinous silica, and alumina without granulating. Poor settling of the acid settlers results for the same reason."

When using in the leach acid strengths up to 30 per cent., the granulating effect mentioned is obtained in an extreme degree. Some investigations on this point indicate that this is really a complex phenomenon involving, first, the solution of silicates to form silicic acid, then the formation of a gel of silica throughout the pulp, the precipitation of ferric hydrate from the entrained ferric sulfate, in the gel, then a syneresis of the gel whereby it separates into two phases, one relatively solid and one extremely dilute. The effects are complicated by concentration changes during the progress of neutralization and by temperature variations. It is hoped to publish later the results of some investigations into this interesting subject.

It may be said, however, that the guiding principle in obtaining good filtration is to dissolve enough silica to make particles of gel stiff enough to stand up under the filtration pressure without deformation; and to precipitate the ferric hydrate inside the particles of gel so that it does not clog the interstices of the cake. In this way, ferric hydrate and gelatinous silica may be played against one another and good filtration secured from a combination of factors, of which one alone might make filtration almost impossible. This represents rather a reversal from the usual attitude. At other electrolytic-zinc plants, it is usual to attempt to keep silica in the calcine as low as possible; and in the case of custom ores, penalties are often imposed if it exceeds a certain figure. When using strong acids, on the other hand, silica becomes desirable, and we have sometimes added oxidized zinc ores to supplement the soluble silica content of low-silica concentrate.

#### ELIMINATION OF COBALT AND NICKEL

A valuable feature of the use of strongly acid leaching solution is in connection with the elimination of cobalt and nickel. These two elements have caused an enormous amount of trouble in zinc electrolysis,

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<sup>29</sup> *Trans.* (1919) 60, 206.

<sup>30</sup> *Op. cit.*

and at least half a dozen methods have been patented for their elimination; Sulman,<sup>31</sup> Fields,<sup>32</sup> Avery,<sup>33</sup> Clevenger.<sup>34</sup>

All of these methods involve either the use of expensive reagents (permanganates, ozone, mercury, beta naphthol, etc.) or the heating of the solutions to a high temperature, or both. The fact that zinc precipitates cobalt and nickel from hot, but not from cold, solutions has been known for a long time. It has been used for the plating of small articles with nickel and cobalt by boiling. The articles are placed in a zinc basket and lowered into the hot solution of cobalt or nickel salts.<sup>35</sup>

The cost of heating up to almost boiling temperature the large volumes of solution used in ordinary low-acid practice is no inconsiderable item. One of the large plants is trying water-tube boilers of the Babcock & Wilcox type, but constructed entirely of copper to withstand the copper-sulfate solutions; they report that the maintenance cost is quite large.

When acid of about 30 per cent. strength is used for leaching, the volume of solution is reduced to about one quarter and at the same time the heat of the reaction brings the solution to the boiling temperature. It is, therefore, only necessary to arrange that this heat is retained until the zinc-dust purification step, in order to care for any cobalt and nickel that may have come in from the ore. In treating zinc concentrate from the Coeur d'Alene district, the purification residues have carried as much as 0.88 per cent. cobalt.

#### RESULTS OBTAINED WITH STRONG ACID LEACHING SOLUTION

The use of a strong acid solution for leaching therefore accomplishes the following results.

1. It permits the treatment of zinc ferrite, which is ordinarily an obstacle in the treatment of low-grade ferruginous concentrates; it enables the roasters to be operated at high capacity.

2. It increases the percentage extraction of both zinc and copper and reduces the amount of zinc in the residues, thereby lowering residue smelting costs.

3. It brings about the solution (and subsequent precipitation) of a large quantity of iron in the leach, and thus thoroughly purifies the solution from arsenic and antimony.

4. It improves filtration and permits the treatment of ores high in soluble silicates which, in low-acid work, would give trouble in filtration from gelatinous silica.

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<sup>31</sup> U. S. Pat. 1334601 (1920); 1336386 (1920).

<sup>32</sup> U. S. Pat. 1382494 (1921).

<sup>33</sup> U. S. Pat. 1347200 (1920).

<sup>34</sup> U. S. Pat. 1283077 (1918); 1283078 (1918).

<sup>35</sup> Georg Langbein (Brant): "Electrodeposition of Metals." H. C. Baird & Co., Inc. New York. 1920.

5. It allows the treatment of ores containing large quantities of cobalt or nickel without the addition of any extra step in the flow sheet.

6. It reduces the quantity of pulp to be agitated and filtered and the volume of solution to be stored and purified, not only in the inverse ratio of the strength of acid used for leaching but to an even greater degree, by the elimination of double leaching, double purification, double filtration, etc. This is of importance not only in the capital cost of the plant but also in operating costs. As pointed out by Elton and Caples,<sup>36</sup> "the double-leaching method requires more labor and equipment, and repair costs are undoubtedly higher especially on the acid filtering equipment." The same writers state that "the operating costs per pound of zinc recovered at the zinc plant were lower with this process (*i. e.*, single leaching) than they have been with the double-leaching scheme."

#### METHODS AND EQUIPMENT DEVELOPED FOR USE IN HIGH-ACID LEACHING

The first stage in the process, that of roasting the zinc concentrate, is a standard operation for which standard roasting equipment may be employed. The roaster at the Martinez plant, Fig. 8, was of the Mc-



FIG. 8.—GENERAL VIEW OF MARTINEZ ZINC PLANT, SHOWING FEED CONVEYORS FROM RAILROAD AND ROASTER STACK ON TOP OF HILL.

Dougall-Wright type, 18 ft. in diameter, with six hearths, and oil fired on the bottom hearth. Temperature on each hearth was measured by a base-metal thermocouple placed about 3 ft. from the wall of the furnace and immediately below the bricks of the hearth above. Temperatures, as measured by this method, were not allowed to exceed 820° C. on account of excessive wear and tear on the furnace; the average temperature on the fifth hearth was 788° C.

<sup>36</sup> Electrolytic Zinc Plant of Anaconda Copper Mining Co. *Trans.* (1920) 64, 758.

The hot calcine was cooled and passed through a 30-mesh trommel screen. The oversize from this screen passed through a small ball mill and returned to the boot of the feed elevator. The screened calcine passed to a magnetic separator situated directly above the calcine bins.

The magnetic separator was of the hollow-pulley type having a row of electromagnets placed inside the pulley at the point at which the ore particles would normally leave the surface of the pulley. The arrangement is represented diagrammatically in Fig. 7. Ore passes under the feed gate, over the small distributing rollers, and on to the large pulley. The magnetic particles are deflected as they fall and, by adjustment of the position of the knife edge, any desired proportion of magnetic and nonmagnetic may be obtained. This type of machine is simple and cheap to install and operate. Undoubtedly closer work could be done by a

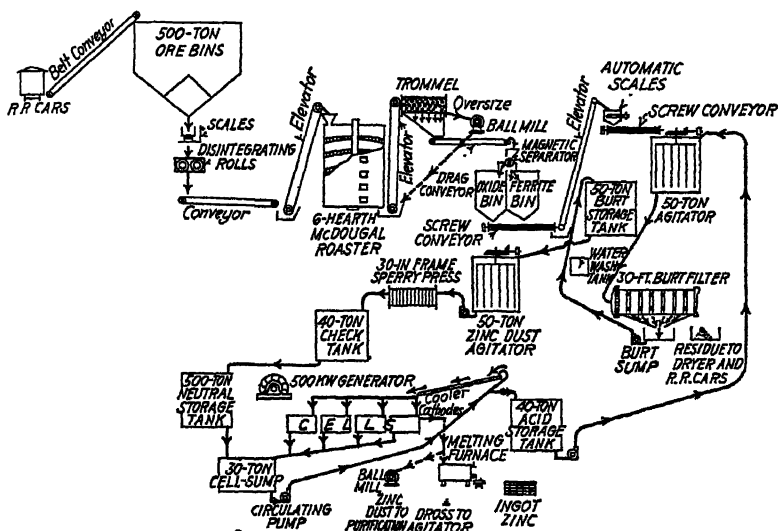


FIG. 9.—FLOW SHEET OF MARTINEZ PLANT.

more elaborate machine but no very sharp separation of oxide and ferrite is aimed at. Cases might arise, however, in which so large a proportion of the zinc was in the form of ferrite that a more perfect separation would be desirable. After separation, the material drops to two bins designated oxide and ferrite, respectively. From these bins the calcine is fed over an automatic weighing machine to the agitators.

The quantity of neutral solution required by the cells, and the quantity of the return electrolyte coming from the cells, amounts to approximately  $5\frac{1}{2}$  fluid tons (of 32 cu. ft. each) per ton of zinc deposited. This return electrolyte carries about 28 per cent. of free sulfuric acid. The neutralization of this acid with calcine brings the temperature of the final pulp close to boiling temperature. It is advantageous, from

the standpoint of coagulating silica, to have the pulp at boiling temperature some little time before the end of the reaction, so the temperature of the leaching solution is raised to about 60° C. before adding ore. The pulp is still practically at boiling temperature when brought down to the filter and most of this heat is retained until the purification is complete and the solution ready to go to the cells. This is done, not as has been sometimes thought, in order to prevent crystallization of the solution (zinc-sulfate solution containing 200 gm. zinc per liter is quite stable at room temperature) but because filtration, purification, etc. are greatly expedited by increase of temperature. For similar reasons, it is customary at other plants to wash filter cakes with hot water (Laist),<sup>37</sup> though in the case of standard low-acid leaching practice, the volume of solution handled is so great that the heating effect due to neutralization of the acid is relatively inconsiderable.

In our flow sheet, Fig. 9, therefore, the only heat required is that necessary to raise the return electrolyte from about 30° C. (cell temperature) to 60° C.; if steam were used for the purpose, it would require about one ton of coal for each 20 tons of zinc produced. In the ordinary way, however, the whole of this heat, as also all heat for wash water, etc., may be obtained from the hot water coming from the roaster cooling system.

### *Leaching Division of Plant*

In the leaching operation, a charge of the warm electrolyte is first introduced into the agitator. This may be either a pachuca, as is used at most other plants, or a flat-bottomed tank with mechanical agitator. Our first work was done with pachucas, but later, we preferred a mechanical agitator because of its lower power requirements and much smaller tendency to cool the pulp. This agitator, if not too large (say, 20 ft. in diameter by 12 ft. deep, and holding at a charge 100 tons of solution, sufficient for the production of about 18 tons of metallic zinc) gives very satisfactory service, though it would probably not be satisfactory for low-acid work as it would hold enough solution for only about  $4\frac{1}{2}$  tons of zinc.

After the return electrolyte is introduced and the agitation started, the door of the ferrite bin is opened and ferrite added to the extent of about one-half of what it is estimated the charge will take. The agitator is then operated for about  $\frac{1}{2}$  hr., when, if necessary, a little ground manganese ore (about 35 per cent. manganese) is added to oxidize the iron.

The gate of the oxide bin is then opened and oxide added steadily until iron in the solution is almost eliminated. This is tested by allowing

a drop of the pulp to fall on a thiocyanate test paper. As long as iron is present, a red ring is obtained. The operator quickly learns by the appearance of this spot to hit the end point with great exactness, so that the last of the iron hydrolyzes out without adding more calcine, leaving a solution still slightly acid.

Before the charge is brought down to the filter, a sample is filtered on a small vacuum filter funnel and the filtrate tested with permanganate to make sure all iron is oxidized. This test also insures that the charge is not over run, because if too much calcine has been added it is detected by the filtrate showing a milky appearance, due to the separation of basic salts.

The pulp then gravitates to the filters. No thickener is required (unless the calcine is very high in zinc) because of the small initial volume

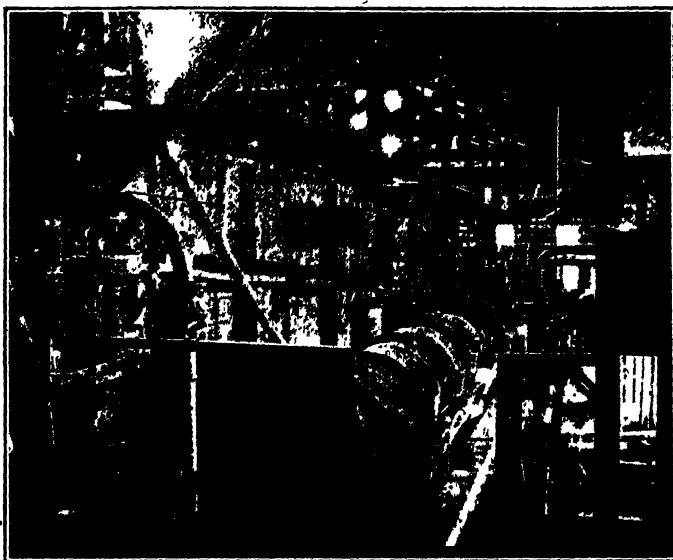


FIG. 10.—FEED END OF BURT FILTER, AT MARTINEZ PLANT.

of solution used. The filter that has been adopted is the Burt revolving pressure type, Fig. 10. Filters of the vacuum type were objectionable for two reasons: In a vacuum filter, one is limited to atmospheric pressure and there is a decided advantage in subjecting gelatinous silica cakes to considerable pressure, as they may be thus, to a large extent, dehydrated. More important, however, is the fact that in a vacuum filter, and indeed in most pressure filters, the cakes must be held on by air pressure after removal from the pulp. During this period, cakes of this kind (*i. e.* containing gelatinous silica) inevitably crack, and then the wash water tends to rush through the channels thus formed. The difficulty of



obtaining washing in this way is shown by the fact that at other zinc plants, where vacuum filters are used, it is necessary to filter and repulp two or three times, and even then a considerable amount of water-soluble zinc is lost in the residues.

In the Burt filter, however, this difficulty is overcome. The rotational movement of the filter keeps a small quantity of pulp always moving over the surface of the cake, and thus cracks are immediately sealed. On this account, the amount of washing required is relatively small; no system of building up wash water is necessary. When using water only, and washing the residues down to 0.5 per cent. water-soluble zinc, the wash water used was not sufficient to make up the water lost by evaporation; therefore the practice of washing residues down to 0.25 per cent. water-soluble zinc was adopted.

The Burt filter is the only one, with which we are acquainted, that could approximate so closely to the ideal of direct replacement of soluble values. This characteristic has found application in the Chile nitrate industry where, after extensive trials of all sorts of filters, some large installations of Burt filters have recently been completed. The problem in this case is somewhat similar—namely, the filtration of a hot concentrated pulp containing valuable solution that should be separated with the minimum of wash water. In connection with the Chile installation of Burt filters, a number of modifications and improvements have been worked out which reduce to a minimum the amount of attention required. One man per shift can attend to three filters, which, when used in the zinc plant will produce from 30 to 45 tons of zinc metal per day.

The Burt filter consists essentially of a steel shell 42 in. inside diameter and 40 ft. long, placed horizontally and supported at one end by a hollow trunnion and at the other end by rollers, as in certain tube mills. The inside of the shell is lined with cotton filter cloth which is sewed round wooden boards about 9 in. wide and 20 ft. long. These boards are held in place by angles bolted to the outside shell. Pulp enters at one end through the hollow trunnion, and residues are discharged at the other end, which is normally kept closed by a circular door, operated by a hydraulic cylinder and a system of toggle levers.

In the ordinary operation of filtering, a charge of pulp is run down until the filter is nearly full. The filter is started revolving, the inlet is then closed, and compressed air put in through the trunnion, thus displacing the solution and leaving the solids uniformly spread over the inside surface of the filter in the form of a cake from 2 to 4 in. thick. The expulsion of all the solution is shown by the blowing of air through the discharge nipples around the shell. A charge of wash water is then run in (with a centrifugal pump) without lowering the pressure inside the filter. The admission of wash water is continued until the cake is washed to the desired point, which is shown by the falling of the specific

gravity of the effluent solution down to some definite point, say 1.05. The addition of wash water is discontinued and the filter allowed to "blow" so that all excess wash water is removed. The pressure is then taken off and the discharge door opened while the filter is still turning. The cake falls to the bottom of the filter, is screwed forward to the discharge end by the angle irons, which are so placed as to form a discontinuous spiral, and falls into the residue cars. When the cake is out, the door is closed, and the cycle repeated. The Burt filter may also be arranged, very conveniently, for a wet discharge. By rotating the filter the cake is repulped with the addition of a small amount of water; the door is then opened and the pulp allowed to flow out.

To prevent dissipation of the heat in the pulp, the outside of the filter is lagged with an asbestos covering. To prevent attack of the iron by the copper sulfate in the solution, the shell is lined with wood, or, when handling solutions very high in copper, with a lead or copper lining. All pipe lines carrying pulp or unpurified solution are of lead, copper, or brass; on the purification side, pipe lines and pumps are of iron. Tanks may also be made of iron but so far, in spite of much investigation, we have found nothing to compare with a lead-lined wooden tank. Even for storage of neutral solution, where plain wooden tanks might seem suitable, it pays well to put in a lead lining; the deterioration on a lead-lined tank is very small whereas that on an unlined wooden tank is high. Again, a wooden tank containing zinc-sulfate solution invariably leaks; this is objectionable not only on account of the waste of solution, but it causes deterioration of sills, concrete floors, etc.

When using strong acids, the volume of solution handled is small, so that the cost of lead lining is a relatively insignificant item. In fact, the cost of the lead lining of tanks throughout the leaching department of the plant would amount, in the ordinary way, to less than 2 per cent. of the total cost of plant. When it is considered that this lead, especially in storage tanks, suffers little deterioration, the advantage of lead lining wooden tanks becomes most obvious.

There has been some discussion as to whether a continuous leaching system is preferable to a batch system. The batch system was chosen because the continuous system, as pointed out by Elton and Caples, is more expensive in labor, repair, and capital charges than the batch method, and the metallurgical exigencies that dictated its adoption elsewhere did not exist in our case.

We have devised a number of simple tests that can be used by the shift men in the plant, so that they do not have to rely on the laboratory for guidance. This system, which gives each operator the means of checking his own work and at the same time definitely places responsibility for any carelessness, greatly improves metallurgical efficiency. These plant tests have been worked out to cover roasting, leaching,

filtration, and purification. At other plants, purification has to be so complete that rather elaborate analytical methods are required to determine whether or not solution is sufficiently pure for electrolysis. In our case, this extreme degree of purification is unnecessary and simple rapid tests can be made by the shifts man on each batch of solution.

Purification is accomplished by agitation of the solution with zinc dust. For making zinc dust, instead of blowing molten zinc with compressed air, as is done elsewhere, we crush cathode zinc in a ball mill, thus avoiding a loss of 5 to 10 per cent. in melting and oxidation. The crushed zinc dust is flaky rather than granular and presents a large surface area.

Speaking generally, the removal of copper and cadmium from solution with zinc dust is not so simple as might at first sight appear. The precipitated copper and cadmium sponge have a strong tendency to oxidize in the presence of air and if this occurs, the oxides, cadmium oxide particularly, tend to go slowly back into solution, either precipitating  $ZnO$  or forming basic zinc sulfate. Once the cadmium sponge is partly oxidized, it is difficult to remove the last traces of cadmium from the solution, as more cadmium tends continually to dissolve. Under these circumstances the only way of effecting a substantial removal of the cadmium is to carry a considerable excess of zinc dust, so as to take care of the cadmium as fast as it comes back into solution.

If air agitation is used for purification, this effect is observed to a marked degree. At Great Falls, where pachucas are employed for the purpose, Laist<sup>38</sup> says "A definite excess of zinc dust is then added to insure that all cadmium is precipitated. The amount of excess dust added is determined by practice and is varied from day to day . . . Like the rest of the process, it must be carefully watched because an error here results in poor tank-room efficiency for several days. The best method is to avoid trouble by using plenty of dust; on the other hand, the use of too much dust is expensive."

When making grade A zinc, it is necessary to remove cadmium from the solution until the amount remaining will not constitute more than 0.05 per cent. of the zinc recovered. At Great Falls where 100 gm. of zinc are taken from each 2 to  $2\frac{1}{2}$  liters of neutral solution, it is necessary to remove cadmium down to about 20 mg. per liter (*i. e.* 50 mg. per 100 gm. of zinc). In our practice, where 100 gm. of zinc are taken from each 500 to 600 c. c. of solution, it is sufficient if solutions are purified down to about 80 mg. cadmium per liter.

The speed of the reaction between the zinc dust and the other metals in solution is greatly accelerated by increased temperature. For this reason we have adopted the system of conserving the heat in the solu-

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<sup>38</sup> *Op. cit.*

tion coming from the filter and also of agitating with zinc dust as far as possible out of contact with air. Not only is oxidation thus minimized, but relatively high temperatures are maintained and reactions occur that would be almost infinitely slow at lower temperatures. The precipitation of cobalt and nickel is a case in point. Another notable reaction is the dissolving of the excess zinc dust in the hot zinc-sulfate solution (yielding hydrogen and basic zinc sulfate). By correcting the basicity of the solution with the addition of a small quantity of return electrolyte, almost all of the zinc dust is brought into solution. This fact has an important bearing on ultimate plant recovery, because in ordinary low-acid practice a considerable amount of zinc is left in the purification residues, necessitating a quite elaborate retreatment system.

After precipitation of copper etc., the solution is clarified through iron filter presses and goes forward to storage whence it is fed into the electrolytic circuit as required.

#### *Electrolyzing Division of Plant*

In the electrolyzing division, what appears to the visitor as the most striking feature of the high-acid practice is the different character of the zinc deposits. The combination of strong acid, high current density, and colloid gives a peculiar type of deposit that can be instantly recognized and distinguished from low-acid zinc (Fig. 11). As Laist says,<sup>39</sup> low-acid zinc is "apt to be porous to some extent and one side is covered with sprouts on raised spots." High-acid zinc, on the other hand, is smooth, homogeneous, and dense. It is even possible to obtain deposits that are bright and lustrous like polished silver and show no apparent trace of crystalline structure. It was, in fact, this remarkable phenomenon (which we stumbled on accidentally) that first drew our attention to the then unexplored combination of strong acids and high current densities.

The theory of this subject is of great interest but it has already been dealt with in other papers, to which those interested are referred. It may be said that the primary factor is the increase in hydrogen overvoltage arising from the high current density. The high overvoltage is maintained by a number of other factors, which tend to keep the deposit smooth and so hold up the current density per unit of surface exposed. Chief among these factors are high solution conductivity, rapid upward circulation of the solution past the cathode (caused by the high current density), and the presence of a colloid that restrains the crystalline growth of the deposit and itself increases hydrogen overvoltage.

Hydrogen overvoltage, in fact, may be said to be the be-all and end-all of electrolytic zinc. A high overvoltage is the be-all, and a

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<sup>39</sup> *Op. cit.*

low one the end-all of the zinc deposit. The finish of a zinc deposit comes as soon as the surface becomes so rough that the current density per unit of exposed surface falls below the critical protective value. Then re-solution sets in.

It has often been assumed that the use of a high current density entails a high power consumption; if the conductivity of the solution is sufficiently high, this is not the case. For example, the average voltage drop across one of our cells at 100 amp. per sq. ft. and 28 per cent. acid is 3.6 volts. According to Laist, the voltage at Great Falls at 30 amp.

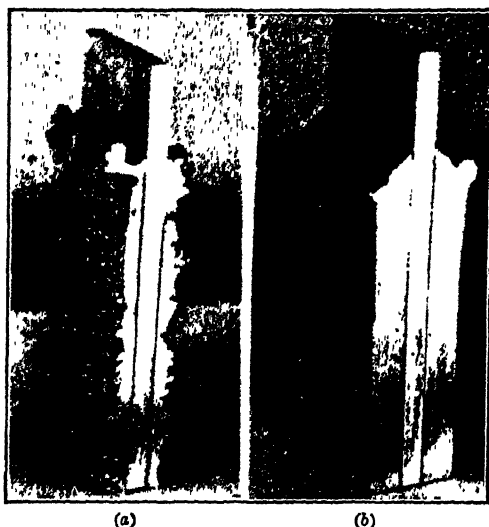


FIG. 11.—SECTIONS OF ALUMINUM CATHODE SHEETS AT SOLUTION LINE, SHOWING DEPOSITS BEFORE STRIPPING. (a) TYPICAL 48-HR. LOW-ACID ZINC DEPOSIT; (b) TYPICAL 24-HR. HIGH-ACID ZINC DEPOSIT.

per sq. ft. and 10 per cent. acid (*i. e.* maximum conductivity) is 3.8 volts. Assuming equal current efficiencies, therefore, the high-acid conditions would show an advantage, although a slight one. As a matter of fact, the current efficiency in the low-acid electrolyte is usually rather low (as Laist says 75 per cent. is now considered good practice) whereas under high-acid conditions it is usually about 90 per cent. The actual power consumed for this case would therefore be 25 per cent. more at the low current density than at the high.

The question of power consumption in zinc electrolysis, like most other metallurgical problems, is mainly a matter of balancing costs. The zinc-plant manager, by greater purification of solutions, more frequent stripping of cathodes and scraping of anodes, reduction of current density, close attention to feeding of cells, prevention of short circuits, etc., can, at any time, improve on the figures for terminal voltage and current efficiency just quoted. It is simply a question for each

particular case of whether the increased output of zinc and saving in cost of power are sufficient to offset the greater operating costs.

Every zinc-plant operator will agree that by far the most important factors in the ultimate power consumption are the frequency, nature, and extent of cell-room troubles. Some trouble is, of course, to be expected when starting a new plant, and in ordinary low-acid electrolytic-zinc work the margins of safety are so narrow that one is skating on thin ice most of the time. A slight error in the purification department, introducing an amount of impurity so small that its chemical analysis may require 48 hr., will often spoil results in the cell room for several days. When using high-acid conditions, there is less variation in the power consumption per pound of zinc because the electrolysis is much less subject to disturbance. Not only do the conditions of the flow sheet inevitably rid the solutions more completely of impurities (such as arsenic, antimony, and cobalt) but the electrolytic cell is capable of dealing with much larger amounts of impurities in case they should, by any chance, be accidentally introduced.

The increased stability thus conferred has been considered by some competent observers, notably C. A. Hansen, as perhaps the most important of the advantages to be derived from the use of the high-acid process. It makes the operation of the cell room virtually independent of the character of the plant feed and thus permits the treatment of an important class of complex ores that, because of lowness of grade, high iron content, or presence of undesirable elements, are not wanted by either the zinc smelter or the electrolytic-zinc plant.

#### NOVEL FEATURES IN HANDLING OF HIGH CURRENT DENSITIES

The salient features of the apparatus that we favor are briefly given here without describing in detail the large amount of experimental work that has been done. It may be taken for granted, wherever our practice deviates from the standard, that the accepted form has been given a thorough trial and then discarded. At the same time, we must admit that the high-acid process with which we are working has been incompletely explored. So far as we are aware, there have been no operations of any magnitude except under the direct supervision of the writers. Any conclusions that may have been reached by others would therefore have been arrived at without the knowledge of operating details and mechanical equipment here presented for the first time—knowledge representing the result of several years' work and the expenditure of large sums of money. This point is mentioned because there have sometimes appeared statements<sup>40</sup> that might give the erroneous impression that other plants had tested the high-acid process and had

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<sup>40</sup> See footnote 36.

obtained operating results of determinative importance, as compared with the data here presented. Being, therefore, the only workers with operating experience in this field, we feel there are still great advances to be made, as compared with the low-acid process which has been pretty thoroughly worked over for the last 20 years. There are unquestionably big improvements possible in mechanical equipment. We look forward to the time when human labor in the cell room will be almost entirely eliminated.

At the Martinez plant, the electrolytic department consisted of 60 cells in electrical series. There were four cathodes in a cell, each cathode taking 450 amp. Current was furnished by a 500-kw. generator set with 11,000-volt synchronous motor. Cells are preferably of wood with lead lining, Fig. 12. Fixed inside the cell is a set of grooved frames in which the cathode sheets slide. These frames are made of wood soaked in

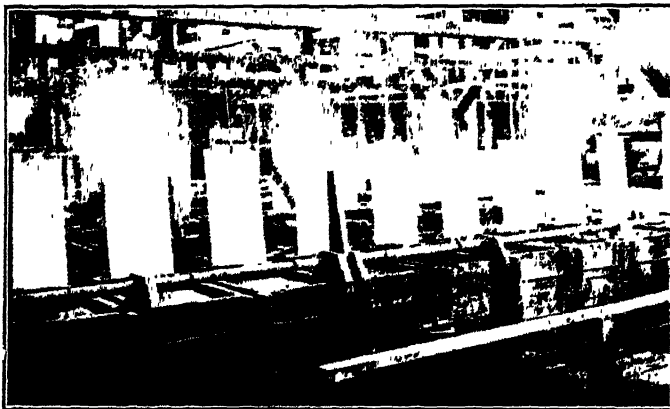


FIG. 12.—PART OF CELL ROOM AT MARTINEZ SHOWING ARRANGEMENT FOR SIMULTANEOUSLY DRAINING ALL CELLS IN CASE OF POWER SHUT-OFF; ALSO ARRANGEMENT FOR LIFTING AND HOLDING OUTCOMING CATHODES UNTIL DRIPPING HAS CEASED.

paraffin wax to protect them against the action of the acid. The grooves are beveled at the top, where they project above the solution, in order to facilitate the introduction of the cathode sheets. When the cathode is in place, it is protected all round the edge for about  $\frac{1}{2}$  in. These frames take the place of the wooden strips ordinarily placed round the edge of the cathode before immersion. The frames eliminate the labor necessary for this operation and, in addition, line up the electrodes accurately in the box, insuring even distribution of current and eliminating short circuits. The anode sheets are made a little larger than the openings in the frames so that it is impossible for them to swing into contact with the cathode. This, together with the relatively small size of the electrodes, makes it possible to carry a much closer spacing of electrodes than would be otherwise possible.

The anodes are of lead; but instead of being made of a plain sheet they are perforated below the solution line so that about 50 per cent. of the area is taken out, Fig. 13. Two of these sheets are used between each cathode so as to make a double anode having a space of about 1 in. between the lead sheets. This arrangement gives reduced terminal voltage, better circulation of solution, and less acid spray in the air. Anodes are hung from a copper bar, lead covered except at one end, where it fits into a tapered slot in the busbar.

This form of contact is also used for the cathodes. After an investigation, which covered all the metals commercially available in sheet form, aluminum sheet was adopted for the cathodes, thereby unwittingly

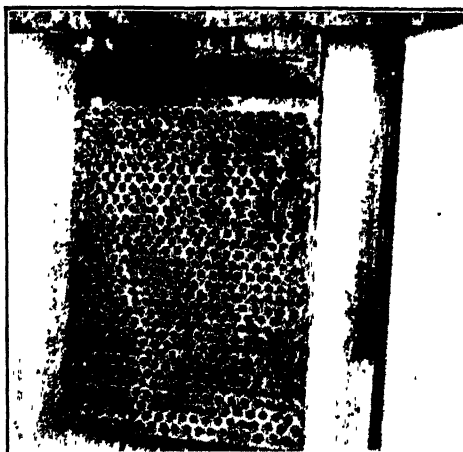


FIG. 13.—TYPE OF ANODE USED FOR HIGH-ACID PROCESS.



FIG. 14.—TYPE OF CATHODE USED FOR HIGH-ACID PROCESS.

confirming the conclusions of Cowper Coles nearly 20 years before, Fig. 14. The proper method of leading in the current gave a good deal of trouble, as it still does at the other plants. Various methods of riveting, soldering, and welding the copper bar to the aluminum sheet were tried, but after a few weeks' service, these joints always gave way and became oxidized, giving rise to hot connections and wasted power. Eventually, at the suggestion of Walter C. Smith, the form shown was adopted; the cathode is cut from a single sheet and the top is rolled over three times to give it rigidity. The tendency of the aluminum to arc on breaking contact was overcome by plating with copper the end that fits into the slot in the busbar. This gives a contact that is always cool and reduces to a minimum the inter-cell busbar loss.

The cathodes at Martinez had an immersed area 14 in. wide and 23 in. long, making a total area of 4.46 sq. ft., counting both sides; the normal



operating current for this cathode is 450 amp. It is doubtful whether it will pay to increase the size of these sheets very much in larger installations on account of the large percentage of the total current that each sheet would take. In the plant now under consideration it is proposed to use a cell circuit of 8000 amp. with ten cathodes, each of 8 sq. ft. immersed area. The active area will measure about 21 in. wide and 27 in. long, and a 24-hr. deposit will weigh about 5.8 lb. per sq. ft. or 46 lb. per cathode.

The stripping of high-acid zinc is remarkably easy. It is well known that stresses are set up in a metal during electrodeposition; and if the metal is sufficiently dense and strong, these stresses may reach a value of several tons to the inch. It is these internal stresses that ultimately cause the detachment of a thick deposit from the starting sheet. On account of the exceptional strength and solidity of high-acid zinc, this phenomenon comes into play and a relatively slight jar is all that is required to cause the two zinc sheets to fall away from the aluminum cathode.

The system of feeding solution to the cells differs from standard practice. The cascade system, usual in electrolytic practice, was tried and abandoned in favor of the method here shown. The solution in the electrolytic circuit is circulated constantly through all cells in parallel, down to a sump, then pumped back to the cells, passing through a cooling system on its way. All neutral solution is fed at one point—the cell sump—and all return electrolyte is withdrawn from the same point. Solution is circulated rapidly and the volume of the cells is so small (on account of the high current density) that the increase in acid strength in passing through a cell is slight. Conditions in all cells are, therefore, kept uniform as to both temperature and acid strength without the necessity of individual attention. This is an important factor from the point of view of both metallurgical performance and operating costs.

The temperature conditions in the cell bring up some interesting points. The energy theoretically required to precipitate one ton of zinc from any sulfate solution, assuming no losses, amounts to about 1760 kw.-hr. per ton of zinc. All energy used in excess of this amount will appear as heat and, unless this heat is in some way dissipated, the temperature of the electrolyte will rise rapidly to boiling point.

As hydrogen overvoltage, and consequently current efficiency, falls with increasing temperature, it is necessary to keep the cell temperatures within certain limits. Ralston<sup>41</sup> says: "The conclusion is inevitable that low temperature is most favorable to the operation of the zinc cell." Experience has indicated temperatures of 75°–100° F. as most favorable to good performance. Except in cold weather, the radiation from the cells

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<sup>41</sup> *Loc. cit.*

does not dissipate sufficient heat to keep temperatures down to this point; consequently the practice of cooling the electrolyte in hot weather by means of lead pipes containing cooling water has been universally adopted.

At some plants, these cooling coils are placed in the cells, at others, they are placed in boxes between the cells and the solution is allowed to circulate over them. In our case, the amount of heat to be dissipated for a given output of zinc is less than at other plants and as the cells are much smaller the area exposed to the air is less. This may be advantageous or otherwise according to whether the air temperature is higher or lower than the cell temperature. At Martinez, in summer, the air temperature ranged up to 105° F. with a high humidity; as we were holding cell temperatures below 95° F., heat was actually being absorbed into the cell system from the air.

These high summer temperatures led to high temperatures (up to 85° F.) in the cooling water, and considerable work had to be done to evolve a cooling system that would operate efficiently under these extreme conditions. A peculiar feature of the problem is that the solutions deposit manganese dioxide and calcium sulfate on any cold surface; provision must, therefore, be made for the ready removal of this deposit from any cooling system. Cooling in trickle towers, by coils in the electrolytic cells, and by circulation of the solution through pipes immersed in water were all tried and gave continuous trouble on account of the formation of these deposits. The problem was solved by running the solution down a wide launder in the bottom of which were laid lead pipes supported on wooden slats. The cooling water flowed through the pipes counter to the flow of solution. Any deposit that may form on the pipes can be readily removed by brushing with a stiff broom without interrupting operations. The formation of the deposit may also be reduced or prevented by laying a piece of zinc in contact with the pipes or by applying a small negative voltage, as is done in the prevention of boiler scale.

Each cell must be supplied with sufficient cooled solution to keep its temperature within the required limits. For instance, a cell using 8000 amp. at 3.6 volts will be taking 28.8 kw., of which 18.7 kw. is being chemically absorbed while 10.1 kw. appears as heat. Where the room temperature is substantially less than the cell temperature, a large part of this heat is dissipated by radiation, convection, evaporation, etc. Assume, however, that in very hot weather none of the heat is so dissipated, and it is required to maintain a temperature of not over 95° F. in the cell, and suppose that the water entering the cooler pipes is 65° F. and that the cooled solution fed to the cells is at a temperature of 70° F.; solution then rises 25° F. in its passage through the cell. The heat carried away amounts to 10.1 kw. or 579 B.t.u. per min. Each cell will, therefore, be

kept within the proper limits by the feeding of a little less than 3 gal. per min. of cooled solution at the feed end.

A similar calculation will give the maximum amount of circulating solution and cooling water for any given condition. Solutions are circulated by hard-lead centrifugal pumps of standard design, which work very satisfactorily. The power used amounts, ordinarily, to less than 0.5 per cent. of the electrolytic power used.

During the electrolysis, manganese is precipitated throughout the solution. The precipitation appears to arise as a result of the formation at the anode of permanganic acid, which reacts with manganous sulfate, as in the Volhard determination of manganese. This is shown by the fact that a filtered sample of our cell solution will gradually become turbid with manganese dioxide on standing.

When using low-acid electrolysis, the manganese dioxide is precipitated as a crust on the surface of the anode and gradually raises the resistance of the cell. Laist<sup>42</sup> says "We insist that this manganese dioxide deposit must be removed at least once every six weeks."

This effect does not occur when using high-acid electrolysis and high current density, unless the anodes are allowed to stand in the solution without any current on them. When this happens, the lead-peroxide coating on the anode reacts with the manganous sulfate in the solution to form a crust of  $\text{MnO}_2$  and  $\text{PbSO}_4$ , which adheres to the anode. We encountered this effect at Martinez and for a time did not realize the cause. We were using only three cathodes in a cell where provision had been made for five. One cathode was drawn from each cell at a time, but before it was drawn another cathode was put in place of the empty spaces between the anodes. This meant that the anodes were used intermittently, under which conditions a crust formed over the surface of the anode, which raised the voltage by almost 0.5 volt per cell. When the trouble was diagnosed, arrangements were made to keep the current on the anodes continuously, which immediately corrected the difficulty.

The manganese dioxide comes down in an extremely fine state of division at the bottom of the cells. Provision was made at Martinez for occasionally sluicing out, collecting, filtering, washing, and drying this manganese dioxide, which was readily sold for 10 c. per lb. The manganese dioxide produced amounts normally to about 4 per cent. of the weight of the electrolytic zinc.

During the electrolysis, glue solution is added to the electrolyte at the circulation sump to the extent of 3 lb. of glue to the ton of zinc produced. Glue, or some similar colloid, is absolutely essential to the production of smooth deposits of zinc at high current densities, no matter how pure the solutions may be. "In fact the use of colloid in the zinc

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<sup>42</sup> *Op. cit.*

cell rests on a sound scientific basis. It tends to raise the overvoltage of hydrogen both at a zinc surface and at surfaces of other metals—a point of especial importance since all commercial solutions contain relatively considerable quantities of impurities. It restricts the crystalline growth of the metal and thus restrains the formation of “trees” which otherwise form rapidly and, by increasing the surface area, lower the current density and consequently the hydrogen overvoltage of the whole surface.”<sup>43</sup>

The presence of glue, together with the double anodes, also tends to eliminate the nuisance of sulfuric-acid spray or mist in the atmosphere of the cell room. This spray, at low-acid plants, causes considerable deterioration of equipment. Laist states that when aluminum sells for 50 c. per lb., the deterioration of aluminum cathodes from this cause amounts to 75 c. per ton of zinc produced. Elton and Caples<sup>44</sup> attribute this mist to the bursting of hydrogen bubbles caused by the re-solution of zinc, saying that it is “directly proportional to the amount of impurities

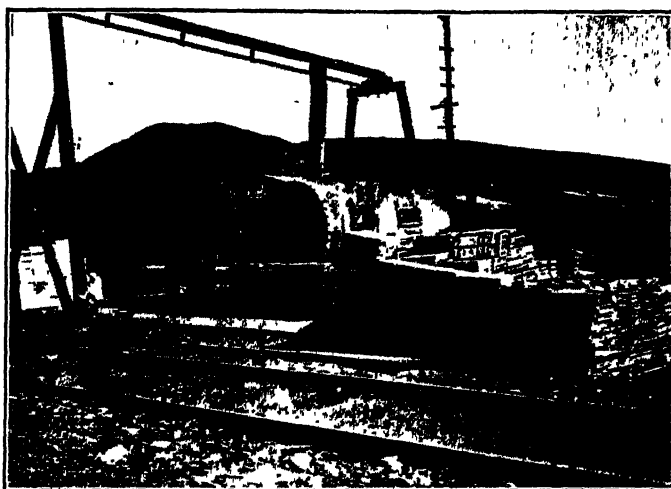


FIG. 15.—OIL-FIRED ZINC-MELTING FURNACE AT MARTINEZ, SHOWING CARLOAD OF ZINC SLABS READY FOR SHIPMENT.

in the electrolyte . . . with pure solution little if any mist is given off.” Laist states that, at Great Falls, “there is at all times a mist of this dilute sulfuric-acid and zinc-sulfate solution in the air.” The use of nose masks by workmen is, therefore, compulsory.

The melting of the zinc cathodes raises some interesting problems. While high-acid zinc, being denser, is easier to melt than low-acid zinc, it is difficult to avoid considerable oxidation unless ammonium chloride be used as a flux. The use of ammonium chloride is objectionable,

<sup>43</sup> See footnote 8.

<sup>44</sup> *Loc. cit.*

because the dross cannot then be returned to the leaching circuit without a purification treatment to eliminate chloride. At the low-acid plants, 4 to 6 per cent. of the gross zinc output goes in this way.

The main problem in the melting of zinc arises from the fact that no matter what sort of a container be used for holding the metal, the zinc oxide tends to form an insulating layer between the zinc metal and the source of heat. Moreover, all electrolytic zinc contains many times its own volume of occluded hydrogen, so that, as the cathodes are pushed below the surface of the molten metal, this gas is evolved and forms a metal froth that oxidizes very readily.

The melting at Martinez was done, intermittently, on lots of about 50 tons of cathodes, using a small oil-fired reverberatory furnace, Fig. 15. No ammonium chloride was used and all dross was returned to the

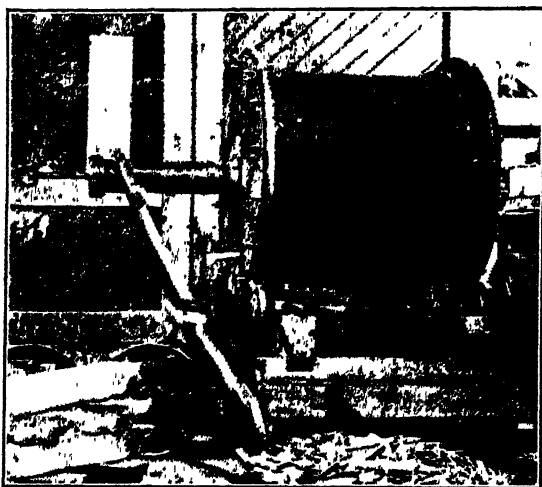


FIG. 16.—THREE-TON ELECTRIC FURNACE OF NEW TYPE AT TEST PLANT OF BUNKER HILL & SULLIVAN MINING Co., KELLOGG, IDA.

leaching circuit. This method, however, was expensive and unsatisfactory because, as soon as it was attempted to obtain any considerable output of zinc from the furnace, temperatures had to be raised and the dross formation then increased.

We have, recently, designed an electric furnace for the melting of cathodes which, though only in the experimental stage, gives promise of eliminating the present weaknesses, Fig. 16. It consists of a cylindrical drum 2 ft. in diameter and 30 in. long lined with firebrick. The heating element consists of a loop of 2-in. calorized iron pipe shaped like a hairpin, the two ends of the loop being brought out through a circular plate of transite board, which closes a hole in the center of the back plate of the drum. The loop is bent at an angle so that it is out of the way of the

zinc feed at the other end of the furnace. The ends of the pipe are connected with an air-cooled transformer stepping down from 2300 volts to 5, 7.5, or 10 volts as required.

The zinc cathodes are passed through a pair of toothed rolls and broken into pieces about 2 in. square. The broken zinc is then fed in by a box-piston type of feeder placed in the center of the other end plate. The furnace can thus be made air-tight except for the air carried in with the broken zinc.

During operation, the drum is continuously rotated, except when zinc is being tapped. In this way, the heat is absorbed by the lining and carried round into contact with the molten zinc, no matter how much dross may be over the surface of the metal. Temperatures throughout the whole system are kept uniform and the danger of any heating or volatilization is avoided. The rolling movement of the drum tends to agglomerate the metallic particles so that what dross is formed is free from shot metal. Results secured show a dross loss of only 2.5 per cent. of the cathode weight and it is expected to improve on this figure when the furnace is made more air-tight.

This type of furnace appears to have a large capacity and may be arranged for all-mechanical handling of the zinc, as regards feeding, tapping, and casting. On account of the low temperatures involved, there should be a low maintenance cost; neither should the first cost be excessive. Our present data indicate that a 25-ton furnace, complete with transformer, would cost less than \$4000.

#### CAPITAL COST

There is no question that the high capital cost involved in the low-acid plant has been a prime factor in limiting the production of electrolytic zinc in this country to the two large plants (at Great Falls and Trail) that were erected, and paid for, under the stimulus of wartime zinc prices. A recent Mines Bureau bulletin<sup>45</sup> thus expresses it: "With the perfection and standardization of the electrolytic process has come a better realization of its limitations, especially the necessity for large-scale operation and the difficulty of obtaining high extraction."

With the high-acid process, the capital cost can be materially reduced. We have already quoted the Anaconda experience, which indicates that the roaster installation cost for a given zinc output will be reduced not only on account of the higher recovery of zinc but because of the greater capacity that can be obtained from a roasting furnace. As regards the leaching department of the plant, it is only necessary to compare the flow sheet of the high-acid process (consisting of four steps) with that of the low-acid process (with twenty-four steps). Also it should be remembered

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<sup>45</sup> *Op. cit.*

that the quantity of solution handled through the leaching plant, agitators, filters, purification, etc., is from four to eight times as great with the low-acid process as with the high.

In the electrolytic department, increasing the current density four times gives a considerable reduction in size of plant. Hansen says<sup>46</sup> "The cost of the cell room is almost inversely proportional to the current density used." In the power generating department, the lower average power consumption per unit of zinc and the more uniform and stable conditions of electrolysis (allowing a high load factor) tend to give a material reduction in the capital cost for the high-acid process.

It is in improved metallurgical results rather than in lower capital costs that the process finds its greatest justification. Especially is this so in connection with the treatment of the more complex or difficultly separable zinc ores containing excessive amounts of copper, iron, arsenic, antimony, cobalt, or soluble silica. Evidence that the high-acid process possesses certain fundamental chemical advantages in the treatment of these problems has been given here, also that the process can be worked efficiently and continuously in large-scale plant operation.

The point we wish to emphasize, in conclusion, is that the work that has been done has served only to show the extent and the richness of the field. With the advent of other workers and greater experience in operation, results should be obtained as much better than those here given as the performance of, say, the Trail zinc plant today is better than the performance of 6 or 7 years ago. This we hope to demonstrate at the new plant, which the Bunker Hill & Sullivan Mining & Concentrating Co. is to erect in the near future.

#### ACKNOWLEDGMENTS

The authors feel keenly that the work here presented has been made possible only through the collective efforts of a number of enthusiastic friends and loyal helpers. It is impossible here to enumerate all of these, but they wish especially to express their appreciation of the assistance received from the following: F. L. Bosqui, R. W. Ffennell, and A. W. Rogers of the Rand Mines Ltd. of South Africa and the Central Mining & Investment Corporation of London; Charles Butters of Oakland, Calif.; Prof. H. G. Stanley, of the Transvaal School of Mines; Prof. F. G. Donnan of London University; Dr. J. N. Pring of the Royal Arsenal, Woolwich; C. L. Moon of Johannesburg; A. V. Udell of San Francisco, Calif.; Walter C. Smith of Baltimore, Md.; C. A. Hansen of Schenectady, N. Y.; H. E. Keyes and Daniel Bosqui of Seattle, Wash.; Frank M. Smith, Stanley A. Easton, and Wallace G. Woolf of the Bunker Hill & Sullivan Mining & Concentrating Co., Kellogg, Idaho.

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<sup>46</sup> *Op. cit.*

## DISCUSSION

W. G. WOOLF, Kellogg, Ida. (written discussion).—The investigation by the Bunker Hill & Sullivan Mining & Concentrating Co. on the complex zinc-lead-silver ores of the Coeur d'Alene district was undertaken with the thought that the advancement in concentration, attributable in large part to flotation, together with the development of the electro-metallurgy of zinc opened up a metallurgic method by varying combinations of which these ores could be successfully reduced. Within the limits of this discussion, it is impossible to set forth the scope of the experimental work that has been done to determine this. Ores representative of the various types in the district were concentrated in a test mill and the zinc concentrates were treated in an experimental electrolytic zinc plant. In the operation of this experimental zinc plant, following the established practice in operating plants, two difficulties caused by impurities in the zinc concentrates developed: silica gelatinization and the presence of cobalt in excessive amounts.

*Silica Problem.*—When the zinc concentrates were roasted and leached the resulting solutions carried unprecedentedly large amounts of soluble silica, so far as the writer knows. Hansen<sup>47</sup> has said that soluble silica could generally be traced back to naturally oxidized ores or to lime rock, etc., used for the purification of solutions. Considerable work was done to determine the source of the soluble silica, the cause of its formation, and to find means of minimizing the trouble incident to its presence in the zinc plant. The writer had the coöperation of Mr. Hansen for much of this work and it is hoped to publish in the near future the results of this investigation. Among the conclusions, it was found that the soluble silica originated in the roasting operation and that no practical variations of the restricting conditions as regards temperature, time of roasting, permissible air supply, etc., when roasting zinc concentrates, prevented its formation in excessive amounts.

An attempt was made, in the milling of the ores, to eliminate the silica from the zinc concentrate. This was successfully accomplished especially on the types of ore, the component minerals of which are what may be called rather coarsely crystallized. The mineral constituents, however, of some of the complex ores of the Coeur d'Alene district are so minutely subdivided that extremely fine grinding is essential to make them separable.<sup>48</sup> The desire was for a reduction process of sufficient flexibility to treat the concentrates of the grades that would possibly be made in practical milling; and, while every effort was exerted to improve the concentration practice as far as possible, an attempt was

<sup>47</sup> C. A. Hansen: *Electrolytic Zinc. Trans.* (1920) 64, 111.

<sup>48</sup> Wright, Parmallee and Norton. *Bur. of Mines Bull.* 205.



made to secure a zinc-plant process that would not have to depend so closely on the elimination in the concentrate feed of elements deleterious to the electrolytic process. This course was adopted because in the past grade has been the impelling factor in the mining and milling of western lead-zinc ores. The returns from the sale of concentrates have depended so closely on grade, and deductions for elements hurtful to the reduction processes have been so onerous that the concentrator has had to make exceptionally clean concentrates. The inability to do so economically has been an important reason why the more complex deposits have not been exploited. To limit the permissible amount of insoluble below a fixed low percentage shifts the problem from the zinc plant to the concentrator and, in the milling of the microcrystalline ores, throws a heavy burden on the latter.

Our efforts in this direction were frustrated when tests indicated, in the treatment of some of the finely crystallized ores, that an insoluble content of less than 2 per cent. in the concentrate resulted in solutions carrying an excessive quantity of soluble silica, if no other means were taken to cope with the soluble silica than those used in the operating electrolytic zinc plants. A special treatment to condition properly or to eliminate the dissolved silica appeared to be essential.

*Cobalt Impurity.*—Cobalt has been found in all the solutions resulting from the leaching of roasted Coeur d'Alene zinc concentrates. Above a certain amount, cobalt in the electrolyte prevents successful electrolysis. Our experience has been that the solutions above-mentioned contain cobalt in excess of the allowable maximum limit, so that the flow-sheet for a zinc plant deriving its feed entirely from Coeur d'Alene concentrates must provide for the elimination of cobalt at each cycle of the solution through the plant.

In addition to other advantages which this paper has clearly set forth, it was claimed that the Tainton-Pring high-acid high-density process overcomes the difficulties caused by both silica and cobalt; it therefore appeared to be particularly adaptable for the treatment of Coeur d'Alene ores. The paper discusses the results of the treatment of some representative Coeur d'Alene ores by this process at the Martinez plant and mentions tests on other ores from this and other districts carried on in the test plant of the Bunker Hill & Sullivan at Kellogg. In this latter plant, concentrates differing widely in composition have been treated; these contained varying percentages of both silica and cobalt. The concentrates varied from 57 to 20 per cent. zinc, 4 to 35 per cent. lead, 0.5 to 25 per cent. insoluble, and 2.5 to 15 per cent. iron. In Coeur d'Alene concentrates, the smallest amount of cobalt found in the leach solutions was 15 mg. per liter, 30 mg. per liter may be taken as the average, and 150 mg. has been noted. We had a successful run on a concentrate from which was dissolved 300 mg. per liter of cobalt.

*Comparative Advantages of Process.*—The recovery figures for this process, some of which are given in the paper, invite a comparative study of the electrolytic process and the present-day retort process—too lengthy and involved a subject to be more than mentioned here. It appears to the writer that the electrolytic process, with the improvements in practice which he sees imminently realizable, is developed to such a degree that it has a decided advantage over the retort process in treating the highest grade concentrate from the Tri-State field. The difficulty of obtaining high extraction, which has been pointed out as a limitation of the electrolytic process,<sup>49</sup> does not pertain to the high-acid high-density process; indeed, the increased recovery of zinc by that process over that obtained in retort practice is responsible mainly for the statement just made. In a test, in the experimental plant, on a concentrate of 53 per cent. zinc 97 per cent. of this metal was extracted.

The advantage accruing by reason of greater metal recovery increases as the grade of concentrate offered for treatment is lowered. This is true also for the treatment cost, which is lowered for the electrolytic process but increases for the retort process when the grade of concentrate is decreased. One of the known facts about the Tri-State field is that far too much zinc is lost in the mill tailings.<sup>50</sup> As the problem is the separation of blende from flint, it is presumed that in the effort to make standard 60 per cent. concentrates, the mines and mills accept much lower zinc recoveries than they could readily obtain if they made lower grade concentrates. The ability of the future electrolytic-zinc plant to treat lower grade concentrates than is now possible should have a decided influence on the economics of zinc production in this field and should increase its productivity and length of life.

C. A. HANSEN, Schenectady, N. Y. (written discussion).—The writer some time ago ventured some opinions regarding soluble silica in sulfide ores<sup>51</sup> which he has since found reason to modify. Certain finely inter-crystallized lead-zinc sulfide ores from the Constitution mine in the Coeur d'Alenes contained no silica soluble in reasonably concentrated sulfuric acid. These ores, when roasted, yielded excessive amounts of soluble silica in the zinc leaching plant. Some of the silica was unquestionably rendered soluble in the roasters, and there appeared to be sufficient relation between the amounts of silica, lead, and soluble silica in the calcines to warrant the belief that a readily broken down lead silicate was formed in the roasters.

Seven ore samples were roasted simultaneously in a small laboratory muffle for  $3\frac{1}{2}$  hr. at 600–700° C. A second lot of eight samples were

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<sup>49</sup> O'Harra: *Bur. of Mines Bull.* 208.

<sup>50</sup> Coghill and Anderson: *Eng. & Min. Jnl. Pr.*, 116, 321.

<sup>51</sup> *Trans.* (1920) 64, 111..

similarly roasted for 8 hr. at about the same temperatures. The amount of soluble silica obtained was approximately proportional to the product of the silica and lead contents of the respective calcines when a given roasting treatment was involved. The results are given in Table 1, the "calculated soluble silica" being based upon the assumption that

$$(\text{SiO}_2 \times \text{Pb}) \times \text{constant} = \text{soluble silica}$$

This, of course, is merely a questionable application of the mass action law to a condition where equilibrium was not attained nor, perhaps, even remotely approached.

The soluble silica was taken into solution in very dilute sulfuric acid as readily as the zinc oxide.

TABLE 1

Sample	Analysis of Calcine, Per Cent.				Soluble Silica, Per Cent.		
	Zinc		Lead	Silica	Determined	Calculated	
	Total	Soluble					
$\frac{\text{Pb} \times \text{SiO}_2}{70} = \text{soluble silica}$							
Roasted 3½ hr.	1092	37.3	30.6	18.5	8.13	2.7	2.2
	1040	47.0	40.5	12.7	11.75	1.6	2.1
	1127	42.9	39.0	19.4	6.70	1.6	1.9
	1019	44.0	40.4	13.4	7.71	1.7	1.5
	993	44.3	41.7	16.3	3.55	0.7	0.9
	887	52.7	47.7	15.2	1.72	0.6	0.4
	961	59.3	55.4	1.3	3.07	0.3	0.05
$\frac{\text{Pb} \times \text{SiO}_2}{34} = \text{soluble silica}$							
Roasted 8 hr.	200	33.0	29.8	12.8	24.9	10.0	9.4
	220	32.5	29.7	13.8	22.4	9.9	9.1
	316	33.5	30.3	17.0	17.6	9.1	8.8
	306	31.9	29.4	12.2	24.1	7.0	8.3
	226	33.1	30.1	10.7	24.3	9.3	7.7
	66	44.1	40.0	16.3	9.2	4.4	4.4
	1128	40.8	34.2	20.7	7.4	4.7	4.4
	1150	37.3	30.9	23.0	6.1	3.4	4.1

The formation of lead silicate is probably dependent on diffusion of lead oxide (or sulfate) into silica. The rate of reaction at a given temperature is probably proportional to the product of the concentrations of the reacting molecular species but the proportionality constant, denoting the rate of reaction, will certainly decrease with decreasing

contact area between the lead and silica, *i. e.*, with increasing grain or crystal size. It seems to the writer that this is consistent with the observed behavior of the Park City ores, which yield very little soluble silica in spite of the fact that they contain considerable lead and silica, both in large crystal aggregates.

When Tainton and Pring first published their results with extraordinarily high acid concentrations and current densities in zinc electrolysis, in common with others engaged in zinc work at the time, I felt that the data were of little practicable value. To obtain such acid concentrations from initially neutral solutions involved supersaturation at room temperatures, which I believed to be impracticable.

I believed that there were two primary reasons for the Tainton and Pring development, both of them rather unsound: First, it seemed that the high current densities were intended to combat the prevailing opinion that electrolysis was an essentially slow process in spite of the fact that a single 9 by 3 ft. cathode at 25 amp. per sq. ft. current density should remove more than 3 tons of zinc a year, whereas the much more cumbersome retort averages not more than 4 tons per year from higher grade raw materials. Second, the cost of the cell room was considered to be unduly high and increasing the current density from 25 to 100 will decrease the cost of cell room about 50 per cent. But, an electrolytic plant involves investment in both primary power and metallurgical plant. Of the total investment, about 40 per cent. is in the metallurgical plant, including its converter substation. Increasing the current density from 25 to 100 should reduce the total investment by about 6 per cent.—not enough to warrant jeopardizing the entire investment by chasing rainbows. This was an unfortunate judgment and I feel better for having acknowledged it when I saw Tainton at work in his Martinez plant in 1920.

The present paper brings out the essential fact that the high current density is rather incidental; the requirement is a high acid concentration for leaching and the high current density is essential to make the high acid concentrations practicable.

I know, from experience, that hot solutions are better than cold solutions in the leaching plant and that dense solutions are preferable to dilute solutions but I have had no experience with such concentrated solutions as Tainton uses. It seems to me that one of the more important advantages of such concentrated solutions is their tendency to dehydrate colloidal jellies. The amount of water retained in silicic acid precipitated from zinc-sulfate solutions falls off much more rapidly with increasing zinc concentration than I expected from the reported vapor pressures<sup>52</sup> of silica gels and the vapor pressure of zinc-sulfate solutions<sup>53</sup> on the assump-

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<sup>52</sup> Zeigmondy, Bachmann, Stevenson: *Zeit. Anorg. Chem.* (1912) 75, 194.

<sup>53</sup> Landolt Bernstein tables.

tion that the gel and solution would be in vapor pressure equilibrium. The hydrolysis of ferric sulfate in zinc-sulfate solutions is noticeably displaced by a variation of 10 gm. zinc in the range 70 to 100 gm. zinc per liter, hydrolysis being more complete in the more dilute solutions.

The more concentrated solutions of Tainton, perhaps more by reason of high temperature than by reason of high concentration, are more readily purified than colder and more dilute solutions, and the higher yield of zinc per unit volume of solution makes it possible to spend more in thoroughly purifying unit solution volume. I believe that Tainton's solutions are purer than the average commercial electrolyte for this reason. If, in addition to this, the use of the very high acid concentrations and very high current densities render one further immune to the effects of impurities in solution, there is much merit in the process as a whole.

Tainton and Leyson refer to the work of Biltz on the adsorption of arsenic upon ferric hydrate. I published some data on this same phenomenon<sup>54</sup> transcribing the Biltz data for adsorption of arsenic by ferric hydrate in water and comparing them with the adsorption of antimony upon ferric hydrate in zinc-sulfate solutions. I am quite certain that adsorption, not alone on ferric hydrate but on aluminum hydrate and silicic acid to a lesser extent, must be relied on for the elimination of these impurities.

In connection with the use of intermittent filter types in the leaching plant, we used a simple device at Bully Hill for determining when to cut off wash-water supply. We wrapped solder around two incandescent lamp bulb bases until they would sink in solutions of 1.05 and 1.02 specific gravity. These were kept in a small receptacle into which the press filtrate was discharged. So long as both bulbs floated, we paid no attention to the filter; when one sank we stood by for the second bulb to sink and then cut off feed water. This device proved to be both simple and effective.

SELWYN G. BLAYLOCK,\* Trail, B. C., Can. (written discussion).—During 1923, the ampere efficiencies for the Trail zinc plant were 90.53 per cent. in No. 1 tank room and 91.36 per cent. in No. 2. These are the averages for the entire year and were made on 48-hr. cathodes; they include every bit of power put into the plant.

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<sup>54</sup> Am. Electrochem. Soc. *Trans.* (1923) 44, 485.

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## Greenawalt Electrolytic Copper Extraction Process

BY WILLIAM E. GREENAWALT, DENVER, COLO.

(New York Meeting, February, 1924)

EVER since electrolytic copper refining gave promise of success, about a half century ago, efforts have been made to apply the idea to the extraction of copper from its ores. The methods of attack have, usually, been to leach with a dilute acid and then to deposit electrolytically the copper from the resulting solution with the simultaneous regeneration of the solvent used in the process. Many efforts have been made, and many patents have been taken out, both in the United States and abroad, to give this idea practical application, but only within the past few years have the difficulties been surmounted.

Leaching and electrolysis, as applied to copper ores, are among the most promising fields in modern metallurgy. New conditions are arising, which will bring the wet methods into prominence; while high freight rates and increasing cost of fuel will tend to limit smelting to highly favored localities. The possibilities offered by the installation of hydroelectric plants and the greatly enlarged range of power transmission will greatly widen the field of electrolytic methods.

Electrolytic methods are ideally adapted to hydroelectric development, for the load is constant throughout the full twenty-four hours, and the cost of both installation and operation of hydroelectric plants is not appreciably greater when operating for twenty-four hours than when operating for eight or ten hours; whereas, in fuel-power generation, as also in smelting, the cost is more or less in proportion to the fuel and power used. Nevertheless, fuel-power generation presents advantages in electrolytic methods, as the power plant may be located in a favorable place while the leaching and electrolytic plants may be located at the mine.

The ultimate possibilities of the wet methods have yet to be determined. The possibilities of smelting have been thoroughly worked out; there is no unsolved major problem in copper smelting, and it has practically reached the limit of its possibilities. It seems hardly probable that any future improvement, either of method or apparatus, will greatly

add to the economy of smelting. Including converting, smelting is simply a form of concentration and does not yield an end product salable to the ultimate consumer.

The wet methods are making rapid progress. Ultimately, some wet method will be found the most advantageous and will receive general adoption. It is not yet evident what that method will be, but the indications seem to point toward some form of leaching and electrolysis. Much progress has been made in the last ten years in the development of leaching methods; much more remains to be made. One by one prospective ideas pertaining to leaching and electrolysis are being cemented into a comprehensive and practical working process, free from unusual uncertainty either of installation or operation.

In 1912, when my book<sup>1</sup> was published, there was not a single electrolytic copper-extraction plant in successful operation. The book concludes with the following statement.

The prevailing idea, especially in metallurgical literature, seems to be that the hydrometallurgical processes for the extraction of copper are applicable only to low-grade ores. But why limit them to low-grade ores? There is no reason why the wet methods have any limitations, either as to the grade of the ore, or its mineralogical composition, provided the process is chemically adapted. This adaption will, in its ultimate analysis, resolve itself down to the consumption of chemicals, the same as in chlorination, cyanidation, or smelting.

Copper is one of the most readily soluble of all the metals, and one of the most readily precipitated either chemically or electrolytically. Theoretically, the solvent processes, especially the electrolytic processes, offer all that could be desired on ores chemically adapted: close extraction, cheap deposition, copper in its metallic form, saving of the precious metals, the installation of plants at the mine, which may be operated in any unit and without admixture of other ores or fluxes. With these theoretical advantages, it is reasonable to suppose that the chemical methods will ultimately be in as general use for the extraction of copper as the cyanide and chlorination processes now are for the extraction of gold and silver.

Within the past ten years, several large leaching plants have been developed and put into successful operation. Among these are the Chuquicamata plant of the Chile Copper Co., in which more than 15,000 tons of oxidized ore are treated per day, and the plant is to be increased to an annual production of about 225,000,000 lb. of electrolytic copper; and the plant of the New Cornelia Copper Co., at Ajo, Ariz., which has a capacity of 5000 tons of ore per day, with a daily production of 120,000 lb. of electrolytic copper. It is claimed that the Chile Copper Co. is producing the cheapest copper in the world, and that the New Cornelia Copper Co. is producing the cheapest copper in the United States. The Chile Copper Co. cost has recently been given as below 6 c. per pound.

<sup>1</sup> "The Hydrometallurgy of Copper." 1912. McGraw-Hill Book Co. New York, N. Y.

The Magma plant of the Utah Copper Co. has a capacity of 4000 tons per day, using sulfuric acid as the solvent and iron as the precipitant. The average grade of ore treated in these three plants ranges from 1.0 to 2.0 per cent. copper. The Union Minière du Haut Katanga, Belgian Congo, Africa, is considering the installation of a large leaching and electrolytic plant to treat its oxidized ores.

The leaching plants now in operation are confined to low-grade oxidized ores. It is reasonably certain that the methods in use are not applicable to high-grade ores or concentrates, or to low-grade ores containing any considerable amount of iron, without radical modification.

While cheap electric power, in conjunction with relatively high fuel cost, is a favorable condition for economic electric smelting, power consumption for electric smelting is a function of the amount of furnace charge, whereas the power consumption of electrolysis is a function of the amount of copper deposited. Electric smelting, as in the case of fuel smelting, requires fluxes and gives a product, such as matte, that requires additional expensive treatment to produce merchantable copper. In very large-scale electric-smelting tests<sup>2</sup> made at Sulitjelma, Norway, it required about 700 kw.-hr. to smelt a ton of copper ore. The same 700 kw.-hr. used electrolytically at, say, 2 volts per cell and an ampere efficiency approaching 90 per cent., would deposit over 800 lb. of metallic copper from a bivalent solution. It is, therefore, evident that electric smelting can successfully compete with leaching only in case the ore, for chemical or physical reasons, is not amenable to any known leaching process that will extract a high percentage of all the metals without too much preparation and excessive loss of solvent.

With the ever-increasing, centralized, electric-power installation, both hydro and fuel, and the efficient, long-distance, transmission lines, cheap power may be made available in almost all mineralized localities. This, with the highly desirable constancy of electric-power load, is an incentive to use electrolysis as a step for extracting the metal from the ore.

#### METHODS OF EXTRACTING COPPER FROM LEACH SOLUTIONS

The methods of extracting copper from leach solutions in general use or contemplated, in practical application may be classified as follows:

(1) Chemical precipitants: (a) metallic iron, (b) hydrogen sulfide, (c) sulfur dioxide; (2) electrolysis with insoluble anodes.

#### *Precipitation with Metallic Iron*

The precipitation of copper with metallic iron is the favorite method for denuding copper from discarded solutions from copper refineries

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<sup>2</sup> C. S. Witherell and H. E. Skouger: The Westly Electric Furnace for Copper Smelting. *Eng. & Min. Jnl.* (1922) 113, 356.



and mine waters. Its strong appeal is the cheapness and abundance of scrap iron. Its drawbacks, for general use as the main precipitant for a leaching process, are the irreclaimability of the solvent chemical and the iron; also the impure quality of the cement copper produced, which rarely exceeds 80 per cent. copper and is usually below 60 per cent. The precipitated copper is also likely to contain other cementable elements, such as arsenic, antimony, and bismuth. In localities where scrap iron is scarce, sponge iron has been tried or contemplated; but even if sponge iron is made at the leaching plant from iron ores, the extraction costs will still be high, on account of loss of the solvent, which will have to be replaced by purchase or specially manufactured. It is difficult to make sponge iron containing more than 85 per cent. metallic iron; the remaining 15 per cent. is mostly insoluble matter, which lowers the grade of the precipitated copper. Sponge iron, however, being very finely divided, is a quick-acting precipitant. It should not be assumed that any scrap iron may be conveniently used for copper precipitation; ordinary scrap iron is objectionable and many of the largest copper leaching plants use scrap "tin."

Whatever kind of metallic iron is used for copper precipitation, both the acid and ferric salts in the leach solutions must be practically neutralized at the expense of the metallic iron before the copper can be effectively precipitated. With neutral solutions, it takes, in practice, about 1.0 lb. of iron to precipitate 1.0 lb. of copper; and in acid solutions, like those rejected from electrolytic extraction plants, it takes about 2.0 lb. of iron to precipitate 1.0 lb. of copper. The theoretical equivalents are 0.875 lb. of iron per 1.0 lb. of copper.

#### *Precipitation with Hydrogen Sulfide*

Hydrogen sulfide is applicable to sulfate or chloride solutions. For every pound of copper precipitated, as cupric sulfide, from sulfate solutions, 1.45 lb. of acid is regenerated. This is an advantage over iron precipitation and represents considerable saving. The precipitation with hydrogen sulfide is as effective with acid as with neutral solutions; ferric salts, however, are reduced before the copper precipitation is complete. The copper sulfide precipitate is voluminous and has to undergo extra metallurgical treatment to produce high-conductivity metal. Copper sulfide is not a desirable product for fusion refining, but there is no difficulty whatever in converting it into pure copper by electrolysis.

#### *Precipitation with Sulfur Dioxide*

Sulfur dioxide has been repeatedly suggested as a precipitant of copper from sulfate solutions; in fact the Andes Copper Co. contemplates using this on a large scale at its proposed plant at Potrerillos, Chile. Sulfur

dioxide has the advantage that a large quantity of sulfuric acid is generated in addition to that regenerated by the liberation from the copper; the precipitated copper is in a fairly compact and relatively pure form. The disadvantage is that heat and hydrostatic pressure are required to precipitate the copper in metallic form, which greatly complicates the practical application. The precipitation by this method is only partial, hence discarded solutions must be denuded by other methods.

### *Electrolysis with Insoluble Anodes*

In all cases where a chemical precipitant is used, the product is contaminated with some substance that either precipitates with the copper or is present in the precipitant, making extra refining necessary to produce commercially pure copper. It follows, therefore, that leaching and chemical precipitation are not applicable to high-grade ore or concentrates, and it is this field that offers the greatest possibilities in copper metallurgy. In the treatment of high-grade material, the end product must be the electrolytic metal, to make the treatment worth while.

Electrolysis is the ideal method of extracting copper from acid solutions. With simple precautions, it usually produces a highly pure metal, even with an impure electrolyte, and at the same time regenerates the solvent for reuse in leaching. Copper produced by electrolysis is, usually, compactly solid and free from oxide or other occluded material, hence in excellent condition for melting and casting. The hindrances to the use of electrolysis are expensive power and chemical interference. All things considered, the electrolytic method can stand a fairly high power cost without seriously contributing to the cost of producing the metal. With direct current at the exceptionally high cost of 1.0 c. per kw.-hr. (say alternating current at \$80 per kw.-yr.), and a production of 1.25 lb. copper per direct-current kilowatt hour, a production that can easily be maintained, the deposition power cost will be only 0.8 c. per lb. copper, and this 0.8 c. will also produce at least 2.75 lb. acid available for leaching.

Chemical interference may be of two kinds: there may be present in the electrolyte substances that cause rapid corrosion of the anodes; there may be present substances that cause rapid re-solution of the copper or prevent deposition on the cathode.

Uncontrollable or uncorrectable chemical interference is usually the prime cause for the non-use of electrolysis and the selection of a precipitant. So far as anode corrosion is concerned, its remedy is merely finding a satisfactory anode composition. Antimonial-lead anodes give highly satisfactory results under ordinary conditions and are generally used. Carbon anodes give excellent results with chloride

solutions, but their use with sulfate solutions must yet be demonstrated. Magnetite anodes are too fragile and have too high a resistance. Ferro-silicon anodes may be used where lead or carbon anodes are unsuitable. The electrolyte, or copper solutions, at Chuquicamata, Chile, made all of these anodes unsatisfactory; although normally a sulfate solution, it contains nitrates and chlorides. Colin G. Fink<sup>3</sup> developed a suitable anode of an alloy of copper-silicon-lead, which is almost insoluble and has a low counter-electromotive force. Re-solution of the cathode deposit is generally due to a highly effective oxidizing agent in solution, such as ferric salts, nitrates, and chlorides; this action is more intense at high temperatures, say 45° C. It is the practice at Chuquicamata to circulate the electrolyte over cooling towers.

Such elements as can exist in solution in two states of oxidation, as far as possible, should be reduced to the lower state before electrolysis; the common offender of this class of elements is iron.

Next to lime in the ore and iron in the electrolyte, aluminum and zinc are ordinarily the most important factors in the problem. Aluminum acts as an acid consumer but, within reasonable limits, also restrains the solvent action of the ferric iron in redissolving the deposited copper, as was discovered by Addicks.<sup>4</sup> Zinc acts in much the same way, as was pointed out by Middleton.<sup>5</sup> The amounts of injurious elements that an ore may contain before a wet process becomes impractical can only be determined by direct experiment. The acid consumption, per pound of copper extracted, will usually be the determining factor. In the last analysis, the application of an electrolytic process to the treatment of copper ores will usually depend on the cost of the acid, per pound of copper extracted, and the cost of power for the deposition of the copper and acid regeneration.

#### ULTIMATE STANDARD LEACHING PROCESS

Although the leaching solvent and the method of extracting copper from solution selected depend on the particular chemical and physical conditions of the ore deposit, the tendency is to consider first sulfate leaching followed by electrolysis with insoluble anodes. There is no cheaper solvent than sulfuric acid, whether purchased or manufactured at the plant. Electrolysis produces the copper in ideal form and regenerates the acid thereby making the process cyclic.

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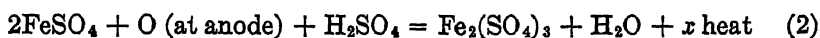
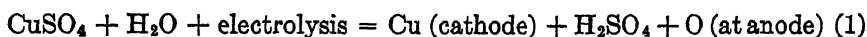
<sup>3</sup> U. S. Pat. No. 1441568.

<sup>4</sup> Lawrence Addicks: The Electrolysis of Copper Sulfate Liquors Using Carbon Anodes. *Met. & Chem. Eng.* (1915) 13, 748.

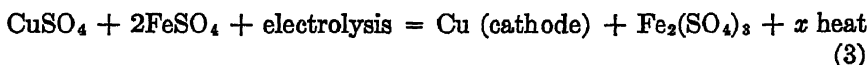
<sup>5</sup> Percy R. Middleton: Electrolytic Deposition of Copper in the Leaching of Roasted Ore and Concentrate. *Min. & Sci. Pr.* (1919) 119, 149.

Most ores amenable to leaching contain two classes of troublesome ingredients: small amounts of alkali earths, which combine easily with sulfuric acid thus causing loss of available acid, and soluble iron. If the alkali earths are in the form of complex silicates that constitute igneous rock gangue, the amount of acid loss may be greatly lessened by avoiding the production of an excessive amount of fines in crushing and avoiding too high acid in leaching; or, if the ore is fine, by reducing the time element to a minimum in leaching.

Soluble iron is the interfering ingredient most frequently encountered in leachable ores, whether non-sulfides or roasted sulfides. Iron in the ferrous condition does little harm and may even be, and probably is, beneficial; but in the ferric condition, it rapidly dissolves metallic copper. During electrolysis, ferrous iron is oxidized to ferric iron by anodic oxidation. The ferric iron so formed, added to that existing before electrolysis, redissolves the copper deposited on the cathode, the iron being reduced back to the ferrous state. The equations of the reactions of electrolysis covering these phenomena are as follows:



Adding equations 1 and 2 overall gives equation 3 for electrolysis with presence of ferrous sulfate,



Then equation 4 for re-resolution,



Adding equations 3 and 4 gives at final equilibrium,



which is to say that when the ferro-ferric cycle is sufficiently energetic and the anodic oxidation complete, no copper is deposited and all the electric power put into the cell is converted into heat.

The quantity  $x$  heat, in equation 3, is not the total energy of reaction; some of the energy liberated is returned to the circuit as electrical energy and manifests itself by lowering the cell voltage—a very desirable feature. The quantity  $y$  heat, of equation 4, is the total energy of reaction; hence all things possible should be done to prevent re-resolution of the deposited copper. All heat liberated raises the temperature of the electrolysis, which in turn accelerates the ferro-ferric cycle.

At constant temperature, the rate of cathodic re-resolution is approximately proportional to the ferric iron in the electrolyte (or catholyte when diaphragms are used). Hence, it is necessary to maintain the amount of

ferric iron in the electrolyte below the critical point at which the temperature rise, due to liberated heat, is sufficient to accelerate the re-solution out of bounds. Re-solution shows up as a decrease in ampere efficiency. With no effort to cool the electrolyte, as small an amount of ferric iron in the electrolyte as 5 gm. per liter has a marked effect; 10 gm. per liter will make the process questionable; and 13 gm. per liter is certain to make it unprofitable. It is generally conceded that if the

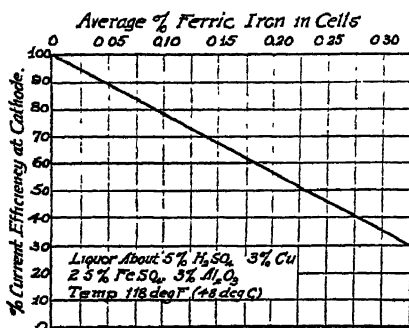


FIG. 1.—EFFECT OF FERRIC SULFATE ON CURRENT EFFICIENCY IN PRACTICE; ACCORDING TO ADDICKS.

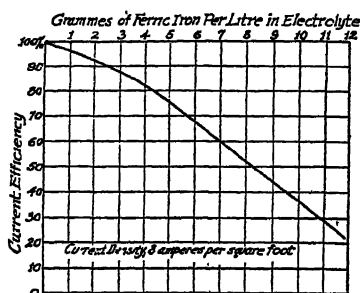


FIG. 2.—EFFECT OF FERRIC IRON ON CURRENT EFFICIENCY; ACCORDING TO MIDDLETON.

ferric iron were thoroughly reduced to the ferrous state, an ampere efficiency could be obtained with a high-iron solution nearly as good as that obtainable with a pure solution; while due to anodic reaction, the energy efficiency with a solution containing a fairly high percentage of ferrous iron may considerably exceed that with a pure solution. Naturally, the lower the ferric iron the better; it should not greatly exceed 2 gm. per liter, although the amount may vary, depending on other conditions such as acidity and temperature; from 1 to 2.5 gm. per liter is amply good.

The graphs, Figs. 1 and 2, show the effect of ferric sulfate on the electrolysis of copper-sulfate solutions containing salts of iron. Both graphs are drawn from experimental data. While they differ somewhat, they show the highly deleterious effects of relatively small amounts of ferric iron in the electrolyte, also the high ampere efficiency obtainable when the ferric iron in the electrolyte is maintained at a very small percentage.

#### *Overcoming Deleterious Effects of Ferric Iron*

The iron, instead of working against the process, should be made to work with it; this is possible if the iron is kept in the ferrous state in the electrolyte. I consider this the fundamental feature in treating copper

ores by leaching and electrolysis and its attainment was one of the objects sought in the development of the process that bears my name. Many methods have been proposed, and some have been tried, for overcoming the deleterious effects of ferric iron in the copper electrolyte; these may be summarized as follows:

1. Interposing a porous diaphragm between the electrodes so as to prevent the ferric salts formed at the anode reaching the cathode.
2. Chemically precipitating the whole or major portion of the iron out of the solution before delivering to the electrolytic department.
3. Periodically, or continuously, diverting a fraction of the cycling solution and denuding it of copper, either electrolytically or by precipitant, or both, before discarding.
4. Maintaining low temperature of electrolyte.
5. Rendering ferric iron harmless, or even useful, by reducing to the ferrous state before electrolysis.

The first method has been tried repeatedly; in fact, the use of porous diaphragms is the first consideration when it is desired to prevent a substance generated within the anolyte from entering the catholyte. But experience with diaphragms in all branches of electrochemistry has been very discouraging, particularly when they are used on a large scale. They lack endurance, increase the cell voltage, obstruct handling, and the slightest rupture causes cessation of proper functioning; besides they are very expensive. Porous diaphragms, in any large electrolytic plant, are only used as a last resort.

The second method has been attempted by carrying the leaching process past neutrality, depending on such basic material as copper oxide or carbonate and lime in the fresh ore for hydrolyzing the iron. But, unfortunately, the ferrous hydrate dissolves completely and the freshly precipitated ferric hydrate dissolves partly in the next addition of acid solution necessary to complete the extraction of copper. So far, it has been found impractical to oxidize and dehydrate the precipitated iron to render it insoluble by subsequent treatment.

The third method is the usual way of limiting any undesirable ingredient that continuously accumulates in the solution. In any closed leaching cycle, there are several such substances; and if the predominating ingredient, from the standpoint of its effect, is taken care of all the other undesirable ingredients are also taken care of. As the discarded solution must eventually contain all ingredients that are not otherwise removed, the solution analysis is ultimately in balance when equal to the quantity discarded divided by the amount of ingredient dissolved from the ore. For example, if the amount of substance  $x$  dissolved from the ore is 4 per cent. of the copper dissolved, and the pregnant solution is electrolyzed from 45 gm. per liter copper down to 15 gm. per liter; and it is desired to limit

the amount of substance  $x$  in solution to 6 gm. per liter, the quantity that should be discarded is  $(45 - 15) \times 0.04 \div 6 = 0.20$ ; or 20 per cent. of the solution cycled between the leaching and the electrolytic departments. A complete elimination by this method is impossible and the method is economically applicable only in case the solution limit is relatively high and the amount dissolved is relatively low.

The fourth method takes advantage of the slow rate of reaction between ferric salts and metallic copper at a low temperature compared with the accelerating faster rates at higher temperatures. It is to be noted that not only do the chemical reactions create heat but also the electrical energy overcoming ohmic resistance within the cell. The Chuquicamata plant, when ferrosilicon anodes were used, had to contend with high iron in the electrolyte, as well as nitrates; as a result, considerable heat was evolved and to avoid an excessive temperature rise the circulation within the electrolytic department was made several times the quantity cycled between the leaching and the electrolytic departments. The solution was electrolyzed in two steps and large cooling towers were placed in both lines of electrolyte flow. Notwithstanding the elaborate equipment of cooling towers, launders, pumps, and pipes it was difficult to keep the temperature of the electrolytic department effluent below 35° C.; at which temperature it is questionable if, even with the absence of nitrates, ferric iron can be allowed to exceed 10 gm. per liter.

Low current density is also resorted to in order to maintain low temperature of electrolyte but at a temperature as low as 30° C. 10 gm. per liter ferric iron will cause re-solution of cathode copper equivalent to more than that theoretically deposited by 1 amp. per sq. ft. of cathode surface, so that nothing is gained in ampere efficiency by going below about 7 amp. per sq. ft. A normal power cost would dictate an economical current density of about 12 amp. per sq. ft. and usual low hydro-electric power cost would warrant using higher current density if ampere efficiency could be maintained reasonably high.

The fifth method solves the difficulty, if the reduction of ferric salts to ferrous salts can be cheaply accomplished and almost all of the iron in the electrolyte maintained in the ferrous state. Whatever the means of reduction, it should be applied continuously to the whole or a large part of the circulating electrolyte. If a fraction of the circulation is diverted, reduced, and then returned, the effect can be calculated in the same manner as described for the third method, diverting and discarding. For example, if the ferric iron derived from all sources, such as direct from the ore, anodic and atmospheric oxidation, etc., is 12 per cent. of the copper deposited; the electrolyte is electrolyzed from 25 gm. per liter copper down to 15 gm. per liter, and 15 per cent. of the electrolyte flow is diverted, completely reduced, and returned to the electrolyte circulation, the ferric iron in the electrolyte will finally amount to  $(25 - 15) \times 0.12 \div$

0.15 = 8 gm. per liter. If all of the electrolyte flow is completely reduced the ferric iron in the electrolyte will amount to  $(25 - 15) \times 0.12 \div 1.00 = 1.2$  gm. per liter.

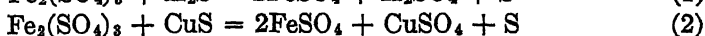
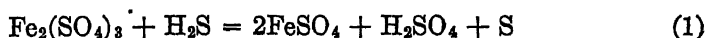
*Reduction of Ferric Salts by Means of Metallic Copper or Hydrogen Sulfide or Copper Sulfide*

There are several ways by which the reduction of ferric salts can be accomplished, but on account of cheapness only the following have received serious consideration, namely: Reduction by means of metallic copper, by means of hydrogen sulfide or copper sulfide, by means of sulfur dioxide.

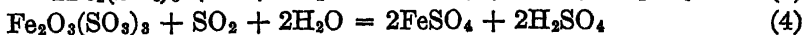
Reduction by metallic copper is possible if metallic copper undesirable for the melting furnaces, produced by denuding discarded solution or decopperizing precipitates, is available. Methods of denuding, such as complete-depositing-out, cementation, etc., generally produce an impure finely divided copper that is much more active than pure massive copper, but with solutions containing less than the desired maximum of 2.5 gm. per liter of ferric iron the rate of reduction, even with the finest cement copper, is much too slow. Also it is impractical to use finely divided metallic copper on the whole electrolyte flow.

Hydrogen sulfide can be used direct for reducing the ferric salts in the electrolyte. Because of the acidity of the electrolyte, the action is preferential in that ferric iron is reduced to the ferrous state before copper sulfide is precipitated, provided the hydrogen sulfide is properly applied. The equations of chemical reaction are as follows:

Primary reactions:



Secondary reactions [substituting  $\text{Fe}_2\text{O}_3(\text{SO}_3)_3$  for  $\text{Fe}_2(\text{SO}_4)_3$ ]:



The sulfur liberated by equations 1 and 2 is, at first, in a molecular state of division; and as the sesqui-oxide of iron is an effective oxidizer and catalyzer some of the elemental sulfur is oxidized to sulfur dioxide, as in equation 3. Then, some of the sulfur dioxide thus produced is oxidized to sulfuric acid, as per equation 4. The secondary reactions take place much slower than the primary reaction, hence they are incomplete, particularly the third reaction, if carried out in an open top-vessel.

The reducing action of hydrogen sulfide may be illustrated by the following experiment: An abundance of the gas was applied, under violent



agitation, to a solution from which the copper had been electrolytically removed from 3.0 to 0.9 per cent. The results were as follows:

	ACID, PER CENT.	COPPER, PER CENT.	TOTAL IRON, PER CENT.	FERRIC IRON PER CENT
Before treatment with $H_2S$ ..	6.10	0.9	0.75	0.35
After 10 sec. treatment.....				0.29
After 20 sec. treatment.....				0.19
After 30 sec. treatment.....				0.12

Some copper was precipitated simultaneously with the reduction of the ferric iron, but the amount was small; and as the  $CuS$  is practically equivalent to the  $H_2S$  for the purpose indicated, it is not likely that the  $CuS$  precipitate would be particularly objectionable.

As some copper solution must be discarded from the system on account of some accumulating ingredient, it would be much more economical to make the hydrogen sulfide play a double role by using it as a precipitant for denuding the discarded solution and then using the copper sulfide precipitate for a reducing agent. The reactions of reduction, using copper sulfide, are the same as with hydrogen sulfide except copper sulfate is produced instead of sulfuric acid, which fits into the process very nicely because the copper sulfate produced conveniently enters the electrolytic department.

Hydrogen sulfide may be applied to wash solutions, thus precipitating copper sulfide and generating an acid wash, which is often desirable for final treatment of ore under leaching. Because of room created by discard and evaporation, the used washes progressively move up in the process and finally join the strong solution that cycles from the leaching department to electrolytic department. If sufficient room is not thus created, some wash solution must be discarded to make room for the final application of clear water. As the ratio of impurities to available acid is greater in the wash solution than in the strong solution, discarding from wash solutions removes more impurities from the system per unit of useful acid wasted. Hydrogen sulfide is an excellent precipitant for dilute solutions.

The practical objection to using hydrogen sulfide, directly or indirectly, for reducing the whole of the ferric iron is that it is somewhat expensive. The major part of the reduction can be done at much less expense by sulfur dioxide. Hydrogen sulfide, however, on account of its very rapid action, is an excellent agent for completing the reduction, if desired, after sulfur dioxide has ceased to function rapidly.

#### *Reduction of Ferric Salts by Means of Sulfur Dioxide*

Sulfur dioxide is the most promising of all the reducing agents. It is effective, if properly used, and at most localities can be cheaply made.

For small quantities, ordinary burning of sulfur by any of the efficient burners offered for sale is satisfactory. The sulfur dioxide thus made is usually of high concentration, and therefore highly effective. For large quantities, roaster gases are the most convenient. In almost all copper mineralized localities, at least some copper sulfide ore can be found either near the deposit being worked, or underlying the oxidized surface of the deposit. The sulfides and oxides are preferably worked together. Sulfide ore, or concentrate, roasted with ordinary care in a McDougall type furnace, will give a gas running over 6 per cent. sulfur dioxide, which gas can be used for reduction. The roasted ore will be in condition for leaching or other metallurgical treatment; therefore if this step of the process is given credit for metallurgical treatment of the sulfide ore, the expense of producing the sulfur dioxide will either be very low or there may be a profit and there would be little reason for economizing on use of the gas.

The sulfur dioxide may be applied to the solution: By injecting either directly into the electrolytic cell or pump-tank or special tank for the purpose; by passing both gas and solution counter-currently through absorption towers; by treating a bulk of solution in a special device, which constitutes a part of the Greenawalt electrolytic copper extraction process.

Injecting a highly corrosive gas into a depth of solution requires an elaborate compressor system, pipes, etc., made of non-corrodable material and requires considerable power for the little useful work done. Also as the bubbles rise through the solution so quickly there is, at any instant, but very little surface of contact between gas and solution and hence very little absorption. This method so far has not given satisfaction.

The use of absorption towers is more rational. In all branches of chemical manufacture, when it is desired to treat a liquid with a gas, the liquid is usually allowed to trickle down through a high tower, meeting the ascending gas. The tower is filled with specially shaped solid material so as to give large surfaces of contact and to obstruct the rapid flow of both liquid and gas. Absorption towers used for reducing ferric iron in copper solutions by sulfur dioxide have not given as good results as were hoped for, even with the use of several towers in series.

The Ajo plant of the New Cornelia Copper Co., in Arizona, is the outstanding example of the use of absorption towers on a large scale for reducing ferric iron. Herewith are given data pertaining to the Ajo plant taken mainly from a paper<sup>6</sup> that has been presented to the Institute.

The equipment consists of three pairs of towers, arranged in series both in reference to the solution flow and to the gas flow. The flows are

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<sup>6</sup> Henry A. Tobelman and James A. Potter: First Year of Leaching by the New Cornelia Copper Co. *Trans.* (1919) 60, 22.

counter-current to each other. The tower packing consists of 11 by  $\frac{3}{8}$ -in. boards set on edge with  $\frac{3}{4}$ -in. spaces between. The first pair of towers that the solution enters are each 28 ft. in diameter by 40 ft. high; the next two pair are each 20 ft. in diameter by 40 ft. high. The solutions are pumped against a 70-ft. head.

## ANALYSIS OF SOLUTION IN AND OUT OF REDUCTION TOWERS

	FERROUS IRON, PER CENT.	FERRIC IRON, PER CENT.	TOTAL RE- DUCTION, PER CENT.	PER CENT OF TOWER CAPACITY
Neutral advance entering towers.....	1.61	0.79		
Solution leaving first pair of towers.....	1.95	0.45	49.5	49.5
Solution leaving second pair of towers....	2.14	0.26	27.5	25.25
Solution leaving third pair of towers....	2.25	0.15	16.0	25.25
Solution leaving settling tank .....	2.30	0.10	7.0	

Between 90 and 100 gal. (340 and 378 liters) of neutral advance solution per minute is used for spray cooling the gas before entering the towers. This solution is practically completely reduced and joins the effluent of the tower system. The following data are for March, 1918.

Average flow through towers, gal. per min.....	1324.0
Average per cent. ferric iron in solution entering towers.....	0.79
Average per cent. ferric iron in solution leaving towers.....	0.17
Average per cent. ferric iron in solution entering tank house.....	0.10
Average per cent. ferric iron in solution leaving tank house.....	0.75
Average per cent. free acid in solution entering towers.....	0.48
Average per cent. free acid in solution leaving towers and entering tank house.....	1.70
Average per cent. free acid in solution leaving tank house.....	2.10
Average per cent. copper in solution entering tank house.....	2.99
Average per cent. copper in solution leaving tank house.....	2.52
Average per cent. copper removed in passing through the tank house.....	0.47
Average number of pounds copper deposited per gross kw.-hr., a.c.	0.76
Average number of pounds copper deposited per gross kw.-hr. 1917- 1918, a.c.....	0.70
Estimated average number of pounds copper deposited per kw.-hr., d.c., March, 1918.....	0.90
Estimated average number of pounds copper deposited per kw.-hr., d.c., 1917-1918.....	0.82
Estimated ampere efficiency, 1917-1918, per cent.....	62.9
Estimated ampere efficiency, March, 1918, per cent.....	70.0
Electrolytic copper shipped, 1917-1918, pounds.....	44,406,695.0
Cement copper shipped as 100 per-cent. copper, 1917-1918, pounds..	14,808,394.0

Total gross volume of towers, cubic meters.....	2819.0
Kilograms ferric iron reduced per minute by towers.....	38.8
Tower volume per liter per minute of solution through towers, cubic meter.....	0.606
Tower volume per kilogram ferric iron reduced per minute in towers, cubic meters.....	72.7
Estimated contact surface per cubic meter of gross tower volume, square meters.....	82.0
Estimated contact surface per kilogram ferric iron reduced per minute in towers, square meters.....	5960.0
Estimated number of pounds of copper deposited per day per cubic foot tower space.....	1.26

At Ajo, the flow through the electrolytic tanks is in parallel; that is, there is no cascading. The total electrolytic circulation is about 25 times that quantity cycled between the electrolytic department and the leaching department and amounts to one liter per minute for about 23 tank-amperes. The net electrolytic oxidation (anode oxidation less cathode reduction) of the ferrous iron is found to be nearly 70 per cent. of the theoretical. Average temperature of the electrolyte is 34° C.; the current density is from 6.20 to 7.56 amp. per sq. ft.

As the amount of copper requiring chemical precipitation is related to the SO<sub>2</sub> reduction of the ferric iron in the electrolyte, the data for iron precipitation are of interest in this connection.

#### SOLUTIONS ENTERING AND LEAVING THE CEMENTATION PLANT, NEW CORNELIA

	H <sub>2</sub> SO <sub>4</sub> , PER CENT.	COPPER, PER CENT.	FERROUS IRON, PER CENT.	FERRIC IRON, PER CENT.	SPECIFIC GRAVITY
Entering.....	2.34	2.12	1.07	1.44	1.31
Leaving.....	0.08	0.02	4.54	0.08	1.25

As surface contact between gas and solution plays so important a role in the reduction of ferric salts, it is natural to resort to a device that will create the maximum surface per unit of bulk of solution treated, while maintaining a large volume of solution saturated with the gas. Fine spraying, or atomizing, it is believed, is the best way to accomplish this condition. An ordinary fine spray or mist, made up of particles 0.03 mm. in diameter, presents 200 sq. m. per liter of liquid in suspension in the gas and settles out of suspension slowly. Fig. 3 illustrates a device for fine spraying while maintaining a large volume of solution saturated with the gas, which constitutes a feature of the Greenawalt process.

#### GREENAWALT ELECTROLYTIC COPPER EXTRACTION PROCESS

The Greenawalt process comprises what is believed to be a number of important steps in the treatment of copper ores by leaching and electrolysis. Its scope may be partly defined by some of the patent claims:

An electrolytic process which consists in electrolyzing copper solutions containing salts of iron to deposit the copper at the cathode with the simultaneous oxidation of the ferrous salts to the ferric salts at the anode, applying a reducing gas to a pool of the electrolyte in a reducing chamber, treating the electrolyte with the gas by intimately mixing the gas with the electrolyte in the pool, maintaining a flow of gas through the reducing chamber, and maintaining a flow of reduced electrolyte from the pool in the reducing chamber to the electrodes and of oxidized electrolyte from the electrodes to the pool.<sup>7</sup>

In electrolytic apparatus, a series of electrolytic units consisting of an electrolyzer and a gasing chamber communicating with the electrolyzer, a gas generator communi-

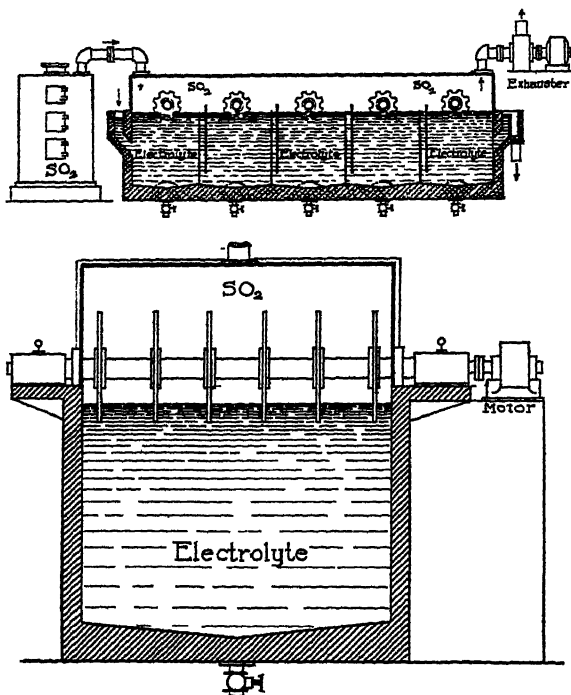


FIG. 3.— $\text{SO}_2$  REDUCER, GREENAWALT PROCESS.

cating with the gasing chamber, means arranged for treating the electrolyte with the gas in the gasing chamber, means for circulating a portion of the electrolyte in a closed circuit between the electrolyzer and the gasing chamber, and means for progressively advancing a portion of the electrolyte from one electrolytic unit to the next of the series.<sup>8</sup>

In the electrolysis of copper-sulfate solutions, the process which consists in applying hydrogen sulfide to the electrolyte.<sup>9</sup>

In the electrolysis of impure copper solutions, the process which consists in precipitating copper from copper solutions with hydrogen sulfide, and applying the sulfide precipitate to the electrolyte as a reducing agent.<sup>10</sup>

<sup>7</sup> U. S. Pat. No. 1314742.

<sup>9</sup> U. S. Pat. No. 1279860.

<sup>8</sup> U. S. Pat. No. 1357493.

<sup>10</sup> U. S. Pat. No. 1340826.

A process of extracting copper from its ores which consists in treating the ore with a dilute acid solution to dissolve the copper, separating the resulting rich copper solution containing salts of iron from the gangue, washing the residue and thus obtaining a lean copper solution, electrolyzing the rich copper solution to deposit the copper with the simultaneous regeneration of acid and ferric salts, chemically precipitating the copper from the lean solution, and then applying the chemical precipitate to the rich copper solution to reduce the ferric salts produced by the electrolysis from a higher to a lower valency.<sup>11</sup>

An electrolytic process which consists in confining a gas over a pool of liquid, treating the liquid of the pool with the gas in the presence of an insoluble substance capable of concentrating or occluding the gas, electrolyzing the liquid, and maintaining a flow of liquid from the electrodes to the pool and from the pool to the electrodes, and progressively advancing the liquid through a series of pools and electrolyzers.<sup>12</sup>

A process of treating sulfide and oxide ores of copper comprising roasting the sulfide ore to make a portion of the copper soluble in water and another portion soluble in dilute acid, leaching the roasted ore with a dilute acid solution, treating the solution with sulfur gas obtained from roasting the sulfide, electrolyzing the solution to deposit the copper with the simultaneous regeneration of acid, returning a portion of the regenerated acid solution to the roasted ore, applying another portion to the oxidized ore, applying a reducing agent to the resulting copper solution from the oxidized ore, electrolyzing the solution to deposit the copper and regenerate acid, returning a portion of the resulting foul acid solution to the oxidized ore, and discarding another portion.<sup>13</sup>

Working within the limits of these claims, it is quite easy to control the process and to remove from 50 to 75 per cent. of the copper from the solution in its passage through the electrolytic plant, and obtain an energy efficiency of at least 1.25 to 1.4 lb. of copper per kw-hr., d.c., with the simultaneous regeneration of from 2.50 to 3.00 lb. of acid, per pound of copper deposited, using lead anodes.

As the process hinges on the successful reduction of ferric iron, this feature of the process will be described first. The ferric iron that builds up in the electrolyte may be reduced to the ferrous state by means, preferably, of sulfur dioxide, copper sulfide, or a combination of these.

### *Sulfur-dioxide Reduction*

Early in the development of the Greenawalt process, it was found that sulfur dioxide, as usually applied, was much too slow in its action. The important factors affecting its action are: Time, temperature, and acidity of solution.

In absorption towers, even with several in series, the solution passes through the system very quickly and, therefore, is in contact with the gases for a very short time. If the solution entering the tower system is neutral, a short period may be sufficient; but if acid, the solution must have a longer time for reduction. Attempts to remedy this condition, by placing a storage tank under the tower and repassing the solution

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<sup>11</sup> U. S. Pat. No. 1345846. <sup>12</sup> U. S. Pat. No. 1375557. <sup>13</sup> U. S. Ser. No. 520241.

down through the tower against the ascending gas, improved results but still the dissolved gas rapidly left the solution, especially if the solution was hot, and it is at the higher temperatures that the reducing action is most effective. Elaborate experiments were made by injecting sulfur dioxide directly into the electrolyte, but even if the electrolyte was maintained saturated with the gas the ferric salts rapidly increased through anodic oxidation.

The outcome of the experimentation was to apply the sulfur dioxide to the electrolyte continuously in a specially designed spray scrubber, in connection with a large pool of the electrolyte and to circulate the electrolyte between the electrolytic cells and reducer pool, so that the solution returning from the reducer was almost completely reduced, or maintained at a minimum predetermined limit. This was accomplished by proportioning the size of pool to the rate of flow so as to give ample time for reduction.

As shown in Fig. 3, the reducer consists of a long rectangular chamber adapted to contain the electrolyte in its lower portion and the gas in the upper portion. Immersed in the gas and making contact with the liquid are rotary disks, or cylinders, mounted on horizontal shafts passing transversely through the chamber. The peripheries of the disks, or cylinders, are usually from  $\frac{1}{4}$  to  $\frac{1}{2}$  in. below the surface of the liquid; and are rotated at from 800 to 1000 r.p.m. A fine spray is thrown up into the sulfur-dioxide atmosphere. The solution inlet and outlet are both trapped, and the outlet is fitted with an adjustable weir so as to adjust depth of disk immersion, even with a variable flow of solution. The solution flows through the reducer in a sinuous stream to prevent short circuiting or stagnation of any of the liquid.

Not only is a large contact surface obtained between spray and gas but also the pool is supersaturated with sulfur dioxide at all times and, as the volume of the pool is large compared with the flow through it, ample time (2 hr. or more) is provided for reduction. No cooling of the solution is necessary; on the contrary the hot gases heat the already warm electrolyte and thus hasten reduction. Any sediment that accumulates in the tank can be easily removed, and the rotary sprayers can be removed and replaced for repairs without interfering with the operation of the reducer. There are no narrow passages to clog up, as in absorption towers, hence there is no particular need of extra effort to remove dust from the gas before use. This same device may also be used for precipitating copper from solutions with hydrogen sulfide.

### *Copper-sulfide Reduction*

Sulfur-dioxide reduction slows down as the acidity of the solution increases. It is not advisable to increase the acidity much beyond 80 gm. per liter for either leaching or electrolysis. In the later stages of

electrolysis, it is usually desirable to use a more positive reducing agent than sulfur dioxide. Hydrogen sulfide, used directly or indirectly, has been found to be the most satisfactory means for reduction in the presence of high acid. The hydrogen sulfide may be generated from low-grade matte or other cheap easily decomposed sulfide and by using denuded waste acid, or it may be generated from sulfur dioxide by heat in the presence of steam and carbon. In all leaching processes, some solutions containing copper or other metals must be wasted. These solutions may be dilute wash water from the ore, or waste foul solutions circulated between the leaching and the electrolytic departments. There is no more satisfactory precipitant for removing copper from discarded solutions than hydrogen sulfide; it can be used whether the solution is strong or weak in either acid or copper, and the precipitation is complete. The precipitate, if produced from an acid solution, is fairly free from noxious impurities. The copper can be separated from the denuded solution by any of the usual settling devices (for example Dorr thickeners) and as the sulfide is next incorporated into a large bulk of solution to be reduced, a relatively thin running pulp may be drawn from the settler. The accumulated residue in the copper-sulfide reducer, including some elemental sulfur produced by the reaction between the copper sulfide and the ferric iron, is removed from time to time. The sulfur may be burned and thereby furnish some sulfur dioxide for the process.

The freshly precipitated copper sulfide is particularly effective in reducing ferric salts. Fused sulfide, copper matte, and natural sulfides are not nearly so effective. Under proper conditions, ferric salts in a low-acid electrolyte can be reduced in less than a minute. In a high-acid electrolyte, agitating with air, the reduction is rapid but not complete. At 50° C., an electrolyte containing 98 gm. per liter free acid, 30 gm. per liter total iron, and 10.4 gm. per liter copper was reduced from 4.5 gm. per liter ferric iron to 1.1 gm. per liter in 5 min.; longer agitation did not improve the reduction.

### *Sulfur-dioxide and Copper-sulfide Reduction*

A general arrangement for a Greenawalt plant, involving both  $\text{SO}_2$  and  $\text{CuS}$  reduction, is shown in Fig. 4. Fig. 5 is a diagrammatic plan as applied to sulfide ores or concentrates. A plant will usually consist of a series of electrolytic units, each comprising a reducer and a group of cells arranged so that the electrolyte will flow in a closed circuit in the respective electrolytic units, while at the same time there is a regular advance flow from one unit to the next of the series and back to the ore. When the solution becomes too high in acid for effective reduction with  $\text{SO}_2$ , the solution is wholly or partly reduced with  $\text{CuS}$ . When the solution becomes too highly charged with soluble salts, a portion is diverted and



the copper precipitated from it and the diverted portion is wasted or put to use.

The general operation of the process may be briefly described as follows, assuming a solution from the leaching department containing

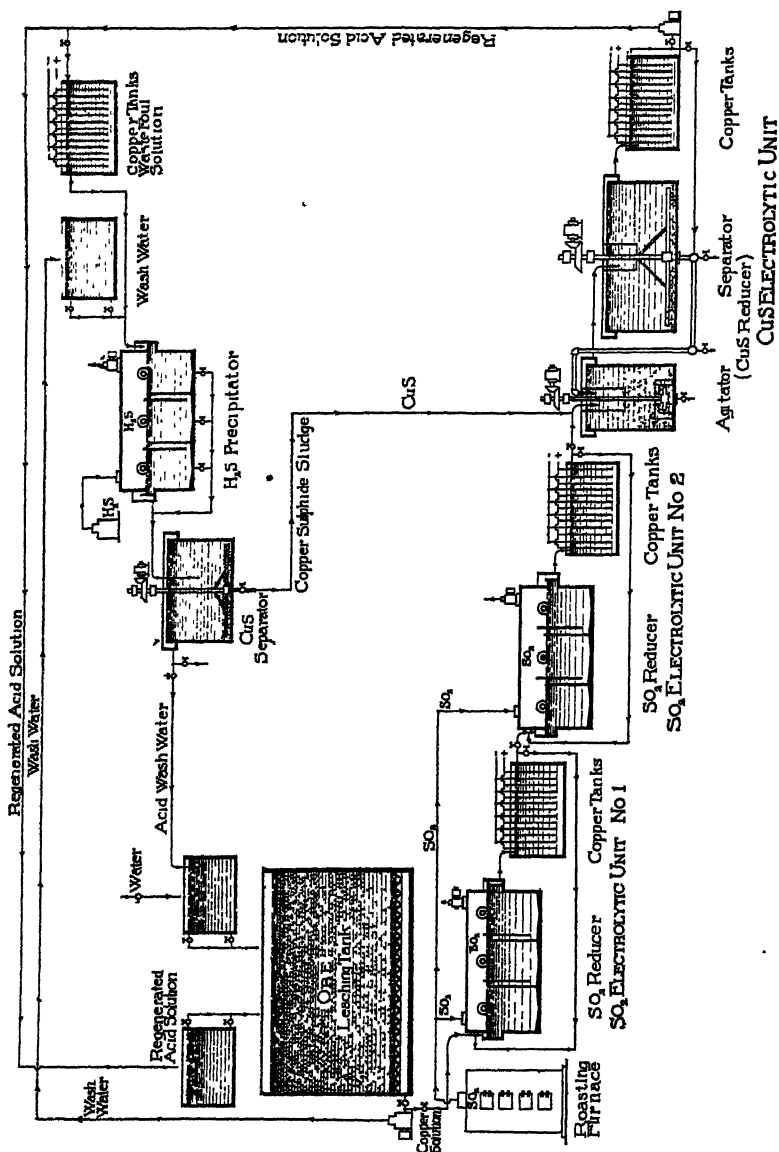


FIG. 4.—DIAGRAMMATIC SECTION GREENAWALT PROCESS.

4.0 per cent. copper and 0.5 per cent. acid, and from 1.5 to 3.5 total iron: This solution flows into SO<sub>2</sub> reducer No. 1 and then to the cells and back again to the reducer, in a closed circuit, until the solution in the first



until the solution shows about 2.25 per cent. copper and about 5.31 per cent. acid. A portion of the electrolyte, the advance flow, is automatically diverted to the third electrolytic unit where the reduction and electrolysis are repeated until the solution shows about 1.75 per cent. copper and 6.69 per cent. acid. A portion of the electrolyte, the advance flow, is automatically diverted to the fourth electrolytic unit which comprises a CuS reducer and a group of cells, and which may also include an SO<sub>2</sub> reducer; here the solution will show about 1.25 per cent. copper and 8.0 per cent. acid. The advance flow is then returned to the ore, but a small portion is diverted for hydrogen sulfide precipitation. This small diverted portion can be reduced to 0.25 per cent. copper, or even 0.10 per cent. by electrolysis, before hydrogen sulfide precipitation, using SO<sub>2</sub> or CuS as the reducing agent; even with a solution containing 10 to 12 per cent. acid. The diverted and electrolyzed portion is treated with hydrogen sulfide to precipitate the copper as CuS, and the barren solution wasted. The CuS precipitate is flowed as a sludge to the CuS reducer of the electrolytic department, where it is used to reduce ferric iron in the electrolyte, while at the same time the copper is recovered as the electrolytic metal. The flow of the solution through the electrolytic plant is entirely automatic; one valve controls the flow from the leaching department through the electrolytic department and back to the leaching department.

The determination of the number of electrolytic units in the deposition of the copper is a matter of discretion. If, for example, it is desired to impoverish a 4.0-per cent. copper solution down to 1.5 per cent., it would not be advisable to flow the 4.0-per cent. head copper solution into a general electrolyte containing about 1.5 per cent. copper and 7.0 per cent. acid, and deposit the copper from such a solution; as would be the case if the series arrangement were not used.

In operation, the amount of ferric iron unreducible, or not readily reducible, with sulfur dioxide increases in the respective units as the electrolyte increases in acidity. In the first electrolytic unit, it is not difficult to maintain the effluent solution from the cells at 0.2 to 0.25 per cent. ferric iron; while in the last unit the ferric iron is likely to range from 0.35 to 0.50 per cent. in the effluent from the cells. It is reasonably certain, however, that the ferric iron that is unreducible, or with great difficulty reducible, in the SO<sub>2</sub> reducers, is also likely to be indifferent toward the copper in the cells.

Copper can be deposited out to as low as 0.15 per cent. in a solution containing from 8.0 to 12.0 per cent. acid, using sulfur dioxide alone as a reducing agent, but with a reduced efficiency. An ampere efficiency of from 50 to 75 per cent. and a power efficiency of about 0.75 lb. copper per kw.-hr. are indicated under these conditions; that is, in impoverishing (or denuding) the electrolyte from about 1.0 per cent. copper down to 0.25 per cent. in special cells. But even this is much cheaper and better

than any chemical precipitation, for the labor of handling the precipitant and the copper precipitate is an expensive item in chemical precipitation. The impure cathodes produced under the conditions indicated are much more easily refined than any chemical copper precipitate. With close electrolytic precipitation of copper from the waste solutions, only a small portion, probably less than 2.5 per cent. of the total copper produced, need be chemically precipitated from the waste electrolyte, while that from the wash waters may make another 2.5 per cent. or a total of 5.0 per cent.

The extent to which it is desirable to impoverish the copper and regenerate acid in the electrolyte before returning it to the ore must be determined for each particular case. The range of economical operation is wide, and it is not likely that these limits will be exceeded.

The great range through which it is possible to electrolyze reduced solutions makes it practical to use sulfate leaching for extracting copper from high-grade ores, roasted concentrates, roasted copper matte, etc. Such material generally runs high in soluble iron, but this is a help to the Greenawalt process.

The presence of a considerable amount of an effective reducing agent, such as ferrous salts, in the electrolyte prevents disintegration of the lead anodes. It also acts as a depolarizer from its avidity for the oxygen produced at the anode; but this latter effect is much more pronounced with the use of carbon anodes. However, carbon anodes have not given satisfaction in sulfate solutions on account of excessive disintegration of the carbon. But as, with effective depolarization, carbon resists disintegration fairly well, there is promise of its successful use in sulfate solutions containing considerable ferrous iron and very little ferric iron. Inasmuch as fully 50 per cent. of the power for deposition could be saved by the successful use of carbon anodes it might be worth while to give carbon anodes a trial under the new conditions. The conditions best adapted to the successful use of carbon anodes are: a high-iron electrolyte with most of the iron in the ferrous condition, a fairly high temperature, low current density, and agitation or rapid circulation.

In the treatment of copper ores by leaching and electrolysis, a number of conditions are encountered, which, while not directly related to the process, are of the most vital importance in its general application. The most evident cases are:

Ores containing copper in the form of both sulfide and oxide, either in the same deposit or in different deposits, which might be subjected to the same or similar metallurgical treatment.

Copper ores, usually as sulfides, which may contain appreciable amounts of precious or other metals, or precious-metal ores containing copper in sufficient amount to make cyaniding prohibitive.

The treatment of sulfide ores by roasting, leaching, and electrolysis presents the most promising field. Acid expense is totally eliminated and the handling of high-grade ore or concentrate involves a minimum expense. If the copper deposit contains both sulfides and oxides, a promising outlook is presented in the treatment of both by a related process. Many mines produce both sulfide and oxide ores, either mixed or at different levels. The sulfide ore, as usual, would be concentrated by any of the ordinary methods, such as by gravity or flotation or both. By making a fairly low-grade concentrate, one say carrying 15 per cent. copper, a fairly high recovery can be made by this preliminary treatment. This is a fairly common and representative condition and, in the operation of the process described, both the sulfide concentrate and the oxidized ore can be treated without any direct acid expense, which is usually the most important factor in the treatment of low-grade oxidized ores.

There is no difficulty by careful roasting in making from 50 to 80 per cent. of the copper water soluble in roasting sulfide concentrate. Assuming a sulfide concentrate containing 15 per cent., or 300 lb., of recoverable copper per ton, 70 per cent. of which can be made water soluble by careful roasting, an acid regeneration of 2.75 lb. per pound of copper deposited by electrolysis, and an acid consumption of 2.00 lb. per pound of copper not soluble in water, the amount of excess acid produced, per ton of concentrate, will be about as follows:

$$\begin{array}{rcl} 300 \text{ lb. copper} \times 2.75 \text{ lb. acid} & = & 825 \text{ lb. acid produced} \\ 70 \text{ lb. copper} \times 2.00 \text{ lb. acid} & = & 140 \text{ lb. acid consumed} \\ \text{Excess acid,} & & \underline{685 \text{ lb.}} \end{array}$$

Assuming, in this connection, an oxidized ore containing 2.0 per cent., or 40 lb., of recoverable copper per ton, with an acid consumption of 3.5 lb. per pound of copper extracted and an acid regeneration by electrolysis of 2.75 lb. per pound of copper deposited, the acid consumed over that regenerated will be about as follows:

$$\begin{array}{rcl} 40 \text{ lb. copper} \times 3.50 \text{ lb. acid} & = & 140 \text{ lb. acid consumed} \\ 40 \text{ lb. copper} \times 2.75 \text{ lb. acid} & = & 110 \text{ lb. acid produced} \\ \text{Acid deficit, per ton ore,} & & \underline{30 \text{ lb.}} \end{array}$$

Dividing 685 lb., the excess acid produced by the treatment of a ton of concentrate, by 30 lb., the acid deficit in treating a ton of oxidized ore, it follows that 22.8 tons of oxidized ore can be treated with the excess acid produced by the treatment of the sulfide concentrate. An ordinary convenient small roasting unit for 25 tons of sulfide concentrate would furnish the sulfur dioxide and acid to leach the 25 tons of roasted concentrate and 560 tons of oxidized ore. If it is not desired to treat oxidized ore, the acid production may be subdued or controlled in various ways, which are well known.

A difficulty of some importance has been encountered in obtaining suitable extractions on copper-sulfide concentrates after roasting. If the concentrate contains precious metals, a low recovery of the copper may seriously interfere with the results desired. Copper concentrates require careful roasting to get an extraction of the copper comparable with that of smelting. Usually roasting will be necessary whether the roasted material is leached or smelted. More careful roasting is required for leaching than for smelting, but the difference in expense is not great. Essentially the same roasting installation will be required for subsequent treatment by either method.

If the concentrate does not contain appreciable amounts of the precious metals, so that the extraction of the copper alone need be considered, it is practical to roast so as to get from 50 to 80 per cent. of the copper water soluble and from 90 to 98 per cent. acid soluble. This would still be a lower recovery than that obtainable by smelting, but the difference could be counterbalanced in the preliminary concentration treatment, where a higher recovery could be made by producing a lower grade concentrate for leaching than would be found most economical for smelting, especially if the concentrate must be shipped to some distant smelting plant. In shipping copper ores or concentrate, it is customary to deduct from 1.0 to 1.5 per cent. (20 to 30 lb. per ton) from the wet copper determination, presumably to cover the smelting loss; this should also cover the loss by leaching.

If the sulfide concentrate contains precious metals in appreciable amounts, provision must be made for their recovery at no excessive cost. This can be done in one of two ways: The tailing from the regular copper leaching may be chlorinated, with chlorine electrolytically produced at the mine, or a special effort may be made to have the copper extraction so complete that the amount remaining in the residue, after thorough washing, will not seriously interfere with the application of cyanide for the extraction of the gold and silver.

If chlorine is used, the extra amount of copper extracted with the chlorine would largely offset the extra expense. The extraction of the precious metals, especially gold, would be exceptionally high, as the previous removal of the copper would leave the precious metals open to easy attack by the chlorine. Assuming the copper to be extracted as the cupric chloride, it will take approximately a pound of chlorine to extract a pound of copper. By the electrolysis of common salt, the cost of the chlorine should not exceed 5 c. per lb., and not much extra chlorine would be consumed in extracting the precious metals. This would leave a wide margin for other expenses of extracting the residual copper, before any appreciable expense could be charged to the recovery of the gold and silver on account of the copper. The copper and the precious metal could be precipitated together, preferably with hydrogen

sulfide, and the copper redissolved from the roasted or unroasted precipitate with acid or ferric iron or both, as already described, thus leaving a high-grade precious-metal precipitate that could easily be freed from copper and refined.

If cyaniding of the copper leach residues should appear more convenient, a double roasting and leaching will produce tailings sufficiently low in copper not to interfere seriously with the cyanide. The double roasting and leaching, while involving an extra expense, would not be prohibitive and would be less expensive than might at first appear, because the first roasting and leaching could be carried out crudely and cheaply without interfering with the ultimate results. That this procedure is effective is evident from the following test:

A flotation concentrate, containing 13.60 per cent. copper, was roasted and leached with inferior results as follows:

	PER CENT. COPPER
Head, roasted concentrate.....	13.60
Acid soluble.....	10.40
Residue.....	3.20

This residue was mixed with about 5 per cent. low-grade pyritic concentrate and reroasted and releached. The results were:

	PER CENT. COPPER
Head, roasted residue.....	3.68
Water soluble.....	3.28
Acid soluble.....	3.34
Tailing.....	0.34

This shows an extraction of about 98 per cent. based on the original ore. The copper leach residue of 0.34 per cent. would not be sufficient to affect cyaniding appreciably, if the ore is well washed.

The problem of recovering precious, or other, metals from copper-bearing ores and concentrates must be considered in any leaching process, if the process is to be generally applicable. Cyaniding of copper leach residues for the extraction of precious metals is preferable to chlorinating if cyaniding is applicable, and especially if the residues contain silver, or gold and silver.

#### DEMONSTRATION TESTS OF GREENAWALT PROCESS

A small experimental plant was installed by one of the larger copper mining companies to try out the Greenawalt process, in a preliminary way. It was arranged that the various steps could be conclusively demonstrated. The work was carried out with the coöperation of the company's superintendent, and with the assistance of the company's engineer. Analyses

were made by the company's chemists. The plant was arranged as shown in the flow plan, Fig. 6, and was adapted for both sulfur-dioxide and copper-sulfide precipitate reduction of the ferric iron formed by the electrolytic deposition of the copper.

The experimental plant consisted, essentially, of a sulfur-dioxide reducer, 3 by 7 ft. in area and 6.25 ft. high. The depth of liquid was

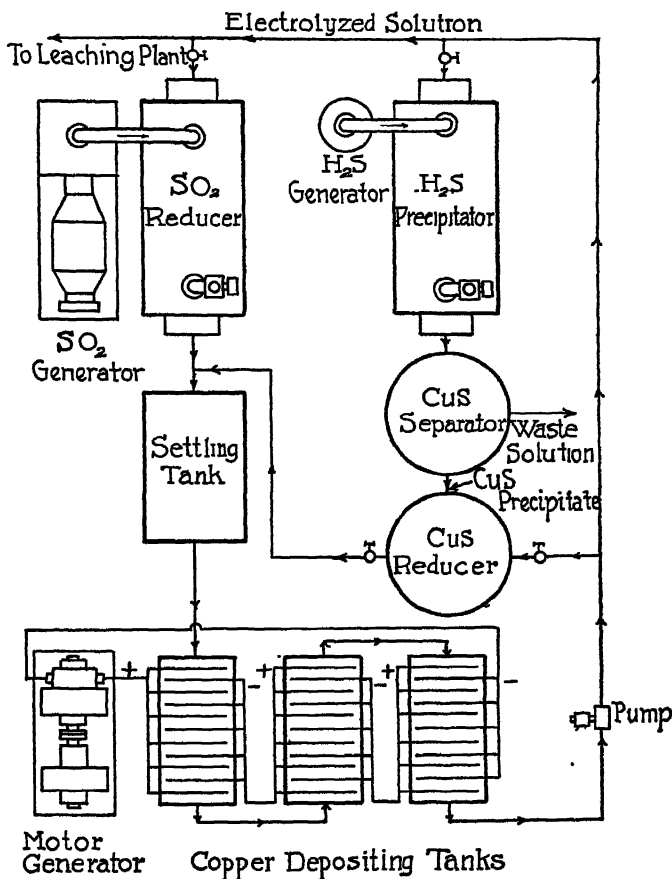


FIG. 6.—FLOW PLAN OF GREENAWALT EXPERIMENTAL PLANT USED FOR TESTS A AND B.

3.5 ft. and the space for the gas above the liquid, 2.75 ft. Four anti-monial-lead disks, 12 in. in diameter, were mounted on a lead-covered shaft and rotated at from 800 to 1000 r.p.m., in the gaseous atmosphere above the liquid, but arranged so that the peripheries had only a slight submergence below the normal surface of the liquid. The liquid level was easily maintained, as shown in Fig. 3, by an ample weir overflow,



which also acted as a seal. The liquid level could be varied by varying the height of the weir. A small rotary sulfur burner, 14 in. in diameter and 30 in. long, supplied the sulfur dioxide. The rapidly rotating disks completely filled the space in the reducers above the liquid with a spray. Some of this spray was as fine as mist, while some was coarse and was thrown the full length of the reducer; open-air tests showed that the spray could be thrown 15 ft. At no time was there any inconvenience from escaping gas; a slight inward suction was easily maintained in the reducer.

There were three electrolytic tanks, or cells, 2.5 by 1.25 by 4.0 ft., arranged in series, for both solution flow and the electric current. The electrodes were arranged for a current density of from 6 to 8 amp. per sq. ft. The current was furnished by a motor-generator set, rated at 175 amp. and from 2 to 8 volts.

The hydrogen-sulfide precipitator was similar to the sulfur-dioxide reducer. The hydrogen sulfide was produced from acid and matte in an ordinary hydrogen sulfide generator 18 in. in diameter and 36 in. high. The copper-sulfide reducer was an ordinary round tank, 5 ft. in diameter and 5 ft. high, in which slowly rotated a wooden paddle to mix the solution and precipitate in the bottom of the tank, while the comparatively clear reduced solution overflowed at the top and was conducted to the cells.

The ammeter readings were taken every 10 min.; the voltmeter readings, across the busbars of the cells, were taken every hour. By taking the voltmeter readings across the busbars, the readings necessarily included the contact resistances between the busbars and the crossbars, and between the crossbars and the electrodes. In this way, all uncertainties in the line were eliminated, while all the resistances in the cells were included. The loss of current and resistance in any line, from the busbars to the direct-current generator, is a matter of design and does not directly enter into electrolytic considerations.

Temperature readings were taken every hour. The copper deposited was carefully weighed at the end of every test, or part, where the test was divided into parts. The volume of solution was kept nearly constant by adding water from time to time to replace that which was evaporated.

#### *Demonstration Test A*

Test A was made to demonstrate the reduction of ferric iron, in a high-iron electrolyte, under increasing acid conditions. The solution flow was maintained at about 600 liters per pound of copper deposited. It was particularly desired to determine the effect of increasing acidity with decreasing copper in the electrolyte, to ascertain to what extent the copper could be removed from the solution before the solution was returned to the ore, which are vital points in the electrolysis of leach copper solutions.

The test, which was continued for 9 days, was divided into four parts, such as might be represented in practice by three-stage reduction and electrolysis, using sulfur dioxide as the reducing agent, while the fourth, or final, reduction was made with precipitated copper sulfide. The solution was obtained from leaching roasted flotation concentrates, and assayed, in part, as follows: Copper, 3.89 per cent.; iron, total, 3.06 per cent.; acid, 1.72 per cent. The results obtained may be summarized as follows:

## SUMMARY, DEMONSTRATION TEST A, SULFUR-DIOXIDE REDUCTION

	PART 1	PART 2	PART 3
Copper in solution at beginning, per cent. . . .	3.89	2.61	1.81
Copper in solution at end, per cent. ....	2.61	1.81	1.04
Copper removed, per cent. ....	33.0	30.7	42.5
Copper removed, based on original, per cent. . .	33.0	53.5	73.3
Acid in solution at beginning, per cent. ....	1.72	4.96	7.85
Acid in solution at end, per cent. ....	4.96	7.85	10.30
Average ferric iron, reducer, first 24 hr., per cent. ....	0.017	0.177	0.35
Average ferric iron, cells, first 24 hr., per cent. .	0.163	0.27	0.37
Average ferric iron, reducer, last 24 hr., per cent	0.10	0.237	0.45
Average ferric iron, cells, last 24 hr., per cent..	0.163	0.343	0.48
Average temperature, degrees C. ....	41.8	42.3	43.0
Average current, amperes. ....	148.2	170.8	162.0
Average voltage across cell busbars. ....	1.76	1.74	1.74
Copper deposited, per 1000 amp.-hr., pounds. .	2.532	2.53	2.162
Ampere efficiency, per cent. ....	97.0	96.9	82.8
Acid regenerated, per pound copper deposited, pounds. ....	2.60	3.61	3.33
Copper deposited, per kilowatt-hour, d.c. at cells, pounds. ....	1.438	1.45	1.25

## GENERAL SUMMARY, TEST A, SULFUR-DIOXIDE REDUCTION

	PARTS 1, 2, AND 3
Copper in solution at beginning of test, per cent. ....	3.89
Copper in solution at end of test, per cent. ....	1.04
Copper removed from solution, per cent. ....	2.85
Percentage of copper removed from solution. ....	73.3
Acid at beginning of test, per cent. ....	1.72
Acid at end of test, per cent. ....	10.30
Copper deposited per 1000 amp.-hr., pounds. ....	2.42
Ampere efficiency, per cent. ....	93.1
Copper deposited per kw.-hr., d.c. at cells, pounds. ....	1.4
Acid regenerated per pound copper deposited, pounds. ....	3.01

It is evident that the best working results would be obtained by stopping the electrolysis when the acidity reaches about 8.0 per cent. and by leaching until the acid in the solution coming from the ore approaches neutrality, instead of containing 1.72 per cent. acid, as in the test.

The solution from part 3, at the end of the sulfur-dioxide reduction test, containing 1.04 per cent. copper, 10.30 per cent. acid, and 0.48 per cent. ferric iron, was treated with copper-sulfide precipitate in an agitator tank with a slowly moving rotary stirrer. The sulfur dioxide had apparently reached its effective limit with the solution containing 10.30 per cent. acid, and part 4 of the test was to determine the reducing action of the copper-sulfide precipitate on this solution.

The solution, before and after treatment with the precipitated copper sulfide, assayed in part as follows:

	BEFORE, PER CENT.	AFTER, PER CENT.
Copper.....	1.04	1.32
Acid.....	10.30	9.16
Ferric iron.....	0.48	0.07
Total iron.....	3.06	3.06

#### SUMMARY OF PART 4 OF TEST A, COPPER-SULFIDE PRECIPITATE REDUCTION

Copper in solution at beginning of test, per cent.....	1.32
Copper in solution at end of test, per cent.....	1.18
Acid at beginning, per cent.....	9.16
Acid at end, per cent.....	9.80
Total copper dissolved from precipitate, pounds.....	40.0
Total copper deposited, pounds.....	30.0
Ferric iron, reduced solution, at start, per cent.....	0.07
Ferric iron, electrolyzed solution, at start, per cent.....	0.24
Ferric iron, reduced solution, at end, per cent.....	0.20
Ferric iron, electrolyzed solution, at end, per cent.....	0.45
Acid produced, per pound copper deposited, pounds.....	2.2
Average current, amperes.....	142.0
Average voltage across busbars of cells.....	1.67
Average temperature, degrees C.....	47.0
Copper deposited, per 1000 amp.-hr., pounds.....	2.12
Ampere efficiency, per cent.....	80.5
Copper deposited, per kw.-hr., d.c. at cells, pounds.....	1.27

The ferric iron in the solution increased quite rapidly from the beginning to the end of the test; with an abundance of copper-sulfide precipitate, the increase should not have been very great. It was thought that the increase of ferric iron was due to the limited amount of copper-sulfide precipitate available for the test. To determine this point, a small amount of the final solution, containing 0.45 per cent. ferric iron was agitated with compressed air, with an abundance of copper-sulfide precipitate, at a temperature of 50° C. The result was as follows:

	FERRIC IRON, PER CENT.	ACID, PER CENT.	TOTAL IRON, PER CENT.
Before treatment.....	0.45	9.80	3.06
After 5 min. treatment.....	0.11		

Further treatment did not increase the reduction. While the reduction is not complete, under very high acid conditions, it would appear probable that the remaining 0.11 per cent. ferric iron, which is not easily further reduced with copper-sulfide precipitate, would be similarly indifferent in redissolving copper from the cathodes in the electrolytic tanks.

Part 4 of test A would indicate that there is no difficulty, either chemically or mechanically, in carrying out this step of the process, under working conditions. The copper-sulfide precipitate, after agitation with the electrolyte, settled quickly. The reduction, in so high an acid solution, under working conditions, while not complete, is rapid. There should be no difficulty in getting effective reduction in any suitable agitator, and a clear overflow in a suitable separator, such as a Dorr thickener. The process would be entirely automatic.

Some interesting design ratios can be derived from test A, although it will be understood that they may not be the best and are in no way final.

#### RATIOS FOR SULFUR-DIOXIDE REDUCER USED IN TEST

Volume of reducer pool, liters.....	2080.0
Rate of solution flow through reducer, liters per minute.....	12.0
Average time passing through reducer, minutes, $2080 \div 12$ .	173.0
Volume of pool per cell-ampere, liters, $2080 \div 480$ .....	4.3
Volume of gas space, cubic meters.....	1.635
Ratio of gas space to volume of pool.....	0.786
Gas space per liter per minute of solution, cubic meter.....	0.136
Gas space per kilogram ferric iron reduced per minute, cubic meters.....	102.0
Total reducer volume, cubic feet.....	131.25
Copper deposited per day per cubic foot of reducer volume, pound.....	0.23

#### *Demonstration Test B*

Test B was made with leach copper solution obtained from the present leaching plant, in the treatment of pyritic residue from acid manufacture. Water containing considerable chlorine is used in leaching the calcines, so that the resulting copper-sulfate solution contains small quantities of chlorine. A partial analysis of the solution used was as follows: Copper, 1.95 per cent.; acid, 0.98 per cent.; total iron, 1.87 per cent.; ferric iron, 0.28 per cent.

The test was divided into two parts. The first part contemplated the deposition of the copper, without any reduction, to see to what extent the accumulation of ferric iron became injurious; and the second part contemplated the use of sulfur dioxide as a reducing agent by the Greenawalt process, to see to what extent the evils of the ferric iron could be corrected after the ferric iron had accumulated in highly injurious amounts. All other conditions remained the same.

## SUMMARY, DEMONSTRATION TEST B

	PART 1 No REDUCTION	PART 2 SO <sub>2</sub> REDUCTION GREENAWALT PROCESS
Copper in solution at beginning, per cent. . . . .	1.95	1.66
Copper in solution at end, per cent. . . . .	1.66	1.03
Acid at beginning, per cent. . . . .	0.93	2.25
Acid at end, per cent. . . . .	2.25	4.75
Acid produced, per pound copper deposited, pounds. . . . .	3.38	3.97
Ferric iron at beginning, per cent. . . . .	0.28	0.06
Ferric iron at end, per cent. . . . .	0.78	0.10
Average temperature, degrees C. . . . .	41.0	45.5
Average current, amperes. . . . .	161.5	157.1
Average voltage across busbars of cells. . . . .	1.84	1.75
Copper deposited per 1000 amp.-hr., pounds. . . . .	1.90	2.79
Copper deposited per kw.-hr., d.c. cells, pounds. . . . .	1.02	1.593
Average ampere efficiency, per cent. . . . .	72.75	106.9

After the first part of the test, and before the copper deposition for second part was started, the solution was given a preliminary reduction with sulfur dioxide in the reducer. The solution was circulated for 3 hr. without electrolysis. A sample of the solution taken from the reducer after 2 hr. treatment showed 0.05 per cent. ferric iron. The reducing action may be compared as follows:

	ICOPPER, PER CENT.	ACID, PER CENT.	FERRIC IRON, PER CENT.
Before SO <sub>2</sub> treatment. . . . .	1.66	2.25	0.78
After 3 hr. SO <sub>2</sub> treatment . . . . .	1.66	2.94	0.06

A comparison of both parts of test B shows the advantages of thorough reduction. The ampere efficiency in the first part is only a little more than half that of the second. The ampere efficiency of over 100 per cent. in the second part is not a mistake, nor is it an inaccuracy; it is due to the small amount of chlorine in the solution, due to leaching with water containing considerable chlorine. The sulfur dioxide in the reducers converts the cupric chloride into the cuprous chloride, and the electric current deposits twice as much copper, per ampere, from cuprous as from cupric solutions. It would appear also, that there would not have been any difficulty in depositing the copper out of the solution to as low as 0.50 per cent. or even 0.25 per cent., with the effective reduction accomplished during this test.

## COMPARISON OF DEMONSTRATION TESTS, WITH OPERATIONS AT NEW CORNELIA

An exceedingly interesting comparison may be made, by comparing the demonstration test A (parts 1 and 2) and (parts 1, 2, 3) with the New Cornelia operations for the year 1918, and for the month of March, 1918, the results of which appear to be considerably above the average.

COMPARISON, NEW CORNELIA RESULTS, 1918, AND MARCH, 1918, WITH  
DEMONSTRATION TEST A

	NEW CORNELIA YEAR 1918	MARCH, 1918	DEMONSTRATION TEST A	
			PARTS 1 AND 2	PARTS 1, 2, AND 3
Copper in solution, beginning, per cent. ....	3.12	2.92	3.89	3.89
Copper in solution at end, per cent. ....	2.71	2.52	1.81	1.04
Copper removed, per cent. ....	0.41	0.47	2.08	2.84
Per cent. copper removed. ....	13.4	15.7	53.5	73.3
Acid at beginning, per cent. ....		1.70	1.72	1.72
Acid at end, per cent. ....		2.1	7.85	10.30
Acid increase, per cent. ....		0.4	6.13	8.58
Ferric iron, beginning, reducers, per cent. ....			0.02	0.02
Ferric iron, at end, cells, per cent. ....			0.44	0.45
Average ferric iron, cell inflow, per cent. ....	0.21	0.09	0.13	0.228
Average ferric iron, cell outflow, per cent. ....	0.82	0.76	0.22	0.293
Copper deposited per kw.-hr., a.c., pounds. ....	0.697	0.76	1.19	1.15
Copper deposited per kw.-hr., d.c., pounds. ....	0.82	0.90	1.44	1.38

This comparison indicates an efficiency, in the copper deposition, of about 50 per cent. by the Greenawalt process over that obtained at the New Cornelia, and with a solution higher in iron, very much higher in acid, and with the removal of 53.5 per cent. and 73.3 per cent. of the copper, as compared with 13.4 per cent. and 15.7 per cent. at the New Cornelia, and with an acid increase of 6.13 per cent. and 8.58 per cent., as compared with 1.62 per cent. at the New Cornelia, before the solution is returned to the ore.

That these results may be attributed to the method employed and not, appreciably at least, to any other cause, may be inferred by comparing the above results at the New Cornelia with test B, in which part 1 may be comparable with the conditions at the New Cornelia. It should be noted, in this connection, that the ferric iron, at the New Cornelia, for 1917, 1918, and to Jan. 1919, is given as follows:

	1917	1918	To 1919
Average ferric iron, inflow, cells, per cent. ....	0.60	0.21	0.254
Average ferric iron, outflow, cells, per cent. ....	1.09	0.84	0.93

In the second part of test B, the same solution was used as at the end of the first part, under practically identical conditions, except that sulfur dioxide was used in the Greenawalt process to reduce the ferric iron. In other words, the increase of efficiency in the second part over the first is directly attributable to the method employed and not to any other cause, and the presumption is that if the same method were applied to the electrolyzed solutions at the New Cornelia, the same results would ensue. While the chlorine in the solution in test B may give a slightly increased copper deposition over the New Cornelia results, nevertheless, the comparison holds so far as part 1 and part 2 are concerned.

## COMPARISON, NEW CORNELIA RESULTS OF 1918, AND MARCH, 1918, WITH DEMONSTRATION TEST B, PART 2

	NEW CORNELIA	NEW CORNELIA	DEMONSTRATION	
	YEAR 1918	MARCH, 1918	TEST B	
	SO <sub>2</sub> RED.	SO <sub>2</sub> RED.	PART 1	PART 2
			NO SO <sub>2</sub>	SO <sub>2</sub> RED.
Copper in solution, beginning, per cent.....	3.12	2.99	1.95	1.66
Copper in solution, at end, per cent.....	2.71	2.52	1.66	1.03
Copper removed, per cent.....	0.41	0.47	0.29	0.63
Per cent. copper removed.....	13.4	15.7	15.0	38.0
Acid at beginning, per cent.....		1.70	0.98	2.25
Acid at end, per cent.....		2.1	2.25	4.75
Acid increase, per cent.....		0.40	1.27	2.50
Total iron, per cent.....		2.40	1.87	1.87
Average ferric iron cell inflow, per cent.....	0.21	0.09	0.28	0.06
Average ferric iron, cell outflow, per cent.....	0.82	0.75	0.78	0.107
Copper per kw.-hr., a.c., pounds.....	0.697	0.76	0.847	1.32
Copper deposited per kw.-hr., d.c., per cent....	0.82	0.92	1.02	1.59

It will be observed that the same increase of efficiency, of about 50 per cent., was obtained in the second part of test B over the first part, as is obtained over the results at the New Cornelia.

*Remarks and Conclusions on the Tests*

At the New Cornelia, the leach solution is passed through seven leaching tanks in series and remains in contact with the ore until the acid is practically neutralized. This solution, containing approximately 3.06 per cent. copper, is then reduced with sulfur dioxide in towers and sent to the tank house, where about 0.44 per cent. of the copper is removed, and the solution returned to the ore, still containing 2.62 per cent., to be again brought up to the standard of about 3.0 per cent. copper going to the electrolytic department. It is believed that the leaching of a 5 to 15-per cent. copper ore or concentrate with such limitations would be impractical. For a 15-per cent. concentrate, it would mean cycling the solution between the leaching and electrolytic departments at least thirty times, which would involve a leaching problem of some magnitude. A low-acid solution will not, ordinarily, give as high an extraction as a high-acid solution. A solution containing 2.63 per cent. copper will not be as active in dissolving copper from the ore under any conditions as a solution containing from 1.0 to 1.5 per cent. copper. A solution low in iron will act more energetically on the iron in the ore than a solution higher in iron.

It will be observed in test A, parts 1 and 2, that the copper content was easily reduced from 3.89 to 1.81 per cent., with an acid content, at the end, of 7.85 per cent., with a high ampere efficiency. This limit of acidity would be desirable for the solution for leaching under any conditions. In parts 1 to 3, the copper content was reduced from 3.89 per cent. to 1.04 per cent., with an acid content at the end of 10.30 per cent.,

with a somewhat lower ampere efficiency. This is probably as high an acid content as it will ever be desirable to use in leaching operations.

It is believed, therefore, that the tests show that any desirable leaching solution can be obtained by the Greenawalt process, and that the solution can be varied at will.

If it is intended to leach copper concentrates, in which a large portion of the copper has been made water soluble, so that the acid regenerated is excessively high, the tests indicate that the copper can be deposited out to as low as 0.25 or 0.50 per cent., using sulfur dioxide alone as a reducing agent, so that even if a large amount of solution is wasted on account of excess acidity, the amount of copper that it would be necessary to precipitate chemically would be comparatively small.

Of course the question arises as to what extent the increased acidity of the spent electrolyte would dissolve from the ore other ingredients than copper. The principal other ingredient is iron and so long as this is kept in the ferrous condition no other harm is done than to increase, probably not excessively, the amount of solution discard.

The treating capacity of the sulfur-dioxide reducer plant can be gathered from the item "Cell-amperes per liters per minute for each reduction treatment." Due to starting the reduction with a much lower ferric iron (2 per cent. vs. 10.3 gm. per liter) and ending at about the same ferric iron (1.3 gm. per liter) in the reduced solution, the Greenawalt method gives about 48 per cent. reduction instead of 87.3 per cent. obtained at Ajo. In consequence, the Greenawalt method would require more reducer-treating capacity per cell-ampere-minute than is indicated by the smaller average ferric iron in the electrolyte; however the figure 40 cell-amperes per liter per minute was taken from test A, wherein was used an experimental reducer of more than ample capacity. It is reasonable to believe that 60 cell-amperes per liter per minute per reduction for the Greenawalt method would give the desired results.

If air only were present in the device used for reducing, a slow oxidation of the ferrous iron would take place; hence, there must be for any set of related conditions a ratio between oxygen and sulfur dioxide in the reducer gas wherein oxidation and reduction are in equilibrium. This ratio must be quite low since the rate of oxidation of ferrous iron by oxygen gas is much slower at all ordinary temperatures than the rate of reduction of ferric iron by sulfur dioxide at the same temperature. Also the solubility of oxygen in water is less than 1 per cent. by weight of the solubility of sulfur dioxide, at temperatures above 40° C., and the reactions take place after the gases are dissolved. It is safe to say that an ordinary dilute roaster gas containing 3 or 4 per cent.  $\text{SO}_2$  will reduce ferrous iron, and gas containing over 6 per cent. would be entirely satisfactory.



Considerably more reducer volume would be required than tower volume, as used at the New Cornelia, but the construction of the reducers would be cheaper per unit volume, and the lift for pumping would be only about one-fifth as high. The solution, instead of being cycled through the electrolytic tanks alone, as in tower reduction, would be cycled through the electrolytic tanks and reducers; that is, the pumping of the solutions, as in the Greenawalt process, would take the place of circulating the solution through the electrolytic tanks and the pumping through towers. It is believed that the power required for circulation and reduction by the Greenawalt method would not exceed that by the tower system as now used.

The roasting of sulfide ore is a necessary step in its metallurgical treatment, and as more sulfide ore can be economically treated than the sulfur-dioxide requirements would warrant, there is no advantage in depleting the  $\text{SO}_2$  contents of the gas to the extent practiced at Ajo.

As before mentioned, when using the Greenawalt method, there would be no need of making a special attempt to cool the roaster gases used for reducing, for the warmer the solution the more rapid and thorough is the reduction of ferric iron and also the lower the cell resistance. Another advantage derived from the hot gases would be the greater evaporation, which would create room for advancing wash solutions, thus making it possible to use more clear water for final wash. The use of hot gases would make it necessary to adapt an acid-proof chamber or flue after the reducer, which would cause a condensation and settling out from the exit gas of a dilute acid solution; this solution can be advantageously added to a dilute wash solution.

#### POSSIBILITIES OF ELECTROLYTIC METHODS

In the consideration of ore-reduction methods and the development of a new process, of the utmost importance are the ultimate possibilities of the process. Assuming practicability, it will usually be found that the process having the greatest theoretical possibilities will be most likely, in the end, to find the widest practical application.

Sulfuric-acid leaching and iron precipitation, for example, have close limitations, for the reason that it takes at least 1.0 lb. of iron to precipitate 1.0 lb. of copper; the acid is neutralized, and none is regenerated for leaching purposes. A minimum fixed charge against the process may reasonably be assumed, therefore, as at least 1.0 lb. of iron, and from 2 to 5 lb. of acid, which has to be purchased or manufactured. Cement copper is the end product. Even if sponge iron can be cheaply produced, the advantage will not be great.

In electrolytic processes, the theoretical limitations approach the border line of perfection; electrolytic copper is produced direct from the

ore, an ampere efficiency closely approaching the theoretical can be obtained, and acid may be regenerated in sufficient amounts, on most ores, to make the process self-sustaining in acid. These results are obtainable, at least with care; the only point to be determined is to what extent they can be realized in large-scale operations.

An electrolytic process, operating on a basis of 1.4 lb. of copper per kw.-hr., d.c., with the regeneration of 3.0 lb. of acid, confines the possibilities of advance within these limits. That there is probability of advance is generally conceded, especially along the lines of depolarization. If carbon anodes can be used in sulfate solutions, it should be quite within the range of probability to deposit 2.5 lb. of copper, per kw.-hr. It has already been demonstrated that the ampere efficiency may closely approach the theoretical, even with a solution containing 3.06 per cent. iron, and that very pure copper can be deposited from impure solutions. If this can be realized in practice, the possibilities for further cost reduction will be confined within narrow limits. The crux of the matter lies in the possibility of using carbon anodes in sulfate solutions; and the possibility of carbon anodes lies in effective depolarization; and effective depolarization lies in effective reduction. On complex ore, sulfate solutions have certain limitations in leaching.

A possibility, in fact a probability, of advance lies in the use of chloride solutions. By the Greenawalt process, as applied to chloride solutions, it should be quite possible to deposit from 4 to 5 lb. of copper per kw.-hr., with the regeneration of an equivalent of acid. It should be remembered that sulfur dioxide reduces the cupric chloride to the cuprous state and the ferric chloride to the ferrous state, and that the electric current deposits twice as much copper from cuprous as from cupric solutions. Years of experimental work with chloride solutions, under these conditions, indicate that the disabilities that apply to carbon anodes, in sulfate solutions, do not apply to chloride solutions containing sulfates. With both cuprous and ferrous chloride acting as depolarizers in the deposition of the copper, the voltage, and consequently the power, may be reduced to a minimum.

In demonstration test A, with effective reduction, using sulfate solutions, 2.5 lb. of copper was deposited per 1000 amp.-hr. With the same ampere efficiency, with a cuprous solution, 5.0 lb. of copper would be deposited. The theoretical e.m.f. required for the deposition of copper from a cuprous-chloride solution, using ferrous iron as a depolarizer, with carbon anodes, is only 0.15 volt, so that 5.0 lb. of copper per kw.-hr. is only about one-sixth of the theoretical. In test A, there was comparatively little depolarization, due to using lead anodes; but this would not apply to a chloride solution, where carbon anodes would have to be used; and if, by the use of carbon anodes the e.m.f. could be reduced to 1 volt, which is within the range of practice, the possibility of depositing

5.0 lb. of copper, per kw.-hr., is by no means visionary. This, coupled with the fact that gold, silver, and small amounts of lead, may be extracted from the ore with the copper, with a chloride solution, presents a theoretical condition, at least, of far-reaching possibilities. What complications may arise in the use of chloride solutions on a large scale remains to be determined; probably none will arise that cannot be surmounted.

#### RECAPITULATION

1. The Greenawalt process offers an effective solution to the high shipping and refining cost of copper ores and concentrates.

2. The process is applicable to sulfides as well as to oxides; to concentrates as well as to the ore direct. It is also applicable to low-gradematte.

3. On suitable ore, it takes the place of smelting the ore to copper matte; of converting the matte into blister copper; and of the ordinary refining process to convert the blister copper into the electrolytic metal.

4. The plants are expensive to install, but they are highly efficient.

5. The process is conveniently applicable to copper matte, if smelting is advisable as a preliminary treatment for ores that are not amenable to direct treatment with an acid solvent.

6. The process is self-sustaining in acid on sulfide ores, on mixed ores, and on high-grade oxidized ores; while on low-grade oxidized ores the amount of acid to be purchased or manufactured is greatly reduced.

7. The deposition of about 1.0 lb. of copper, a.c., or about 1.4 lb. d.c., per kw.-hr., is attainable with the simultaneous regeneration of 3.0 lb. of acid, which is used cyclically in the process.

8. On the basis of 1.0 c. per kw.-hr., a.c., for power, the power cost for the deposition of 1.0 lb. of copper and the regeneration of 3.0 lb. of acid, would be 1.0 c. The total power cost will be about 1.10 c. per lb. of electrolytic copper produced.

9. Power is one of the principal items of expense, both of installation and operation, and cheap power, within transmittable distance, is an important factor in the production of cheap copper.

10. The efficiency of copper deposition in any electrolytic extraction process is primarily dependent on the ferric iron in the electrolyte. In the Greenawalt process, by properly proportioning the size of the pools of electrolyte under treatment of the sulfur dioxide and copper sulfide, and the rate of flow, any desired reduction of the ferric iron is obtainable.

11. The copper may be effectively deposited from solutions of any acid content likely to be used in copper leaching.

12. It is possible, by this process, to deposit about 50 per cent. more copper per kw.-hr. than that shown by the published accounts of the large electrolytic copper extraction plants now in operation.

13. The amount of copper requiring chemical precipitation will be only about 5 per cent. of the total copper produced, and this 5 per cent. is converted into the electrolytic metal in the regular operation of the process.

14. There is no uncertain departure of any kind in the application of the process; no unusual or unproved apparatus is used.

15. The entire process can be made practically automatic, and can be carried out mechanically.

16. Copper ores or concentrates containing appreciable amounts of the precious metals can be successfully treated.

17. Metallurgically, the process is independent of the magnitude of operation; plants may be installed and operated in any convenient units.

18. While the process is applicable to low-grade oxidized or sulfide ores, it will probably find its widest application to the treatment of relatively high-grade ore and concentrates.

19. The end product of the process is all in the form of the electrolytic metal, salable direct to the consumer, if it is desired to dispose of it in that way.

## DISCUSSION

STUART CROASDALE, Denver, Colo. (written discussion).—The author has made a decided advance toward solving the ferric-iron problem in copper leaching and electrolytic precipitation. All plants, heretofore, confronted with this problem and using this process have done no more than extract a small percentage of copper from the lixivium during each leaching cycle.

There are few mines of oxidized copper ore in the world where this problem will not arise from the character of the mineral and gangue. The most notable exceptions are the mines of the Chile Copper Co. at Chuquicamata, and possibly the Katanga mines in the Belgian Congo, Africa. At the New Cornelia mine, both the iron oxide and alumina were the resultant products of slow oxidation in an arid region. Both were in what might be termed a "freshly precipitated" condition and were readily soluble in acid of any strength. Neutralizing the lixiviant by means of fresh ore did not remove this difficulty because the precipitated iron oxide was immediately dissolved by any free acid in the succeeding lixiviant. I never believed that any ultimate advantage is gained by reducing the acidity of the lixiviant below 3 per cent., or probably 5 per cent., when the time element, plant capacity, and all other things are considered. The author has demonstrated that he can commercially reduce the ferric iron and obtain a high recovery of the copper from lixiviums containing as much as 8 and 10 per cent. of free acid.

Any oxidized ore derived directly *in situ* from primary sulfides must necessarily be contaminated with a certain amount of sulfide ore. New

Cornelia was no exception for, in places, the sulfide ore came almost to the surface. It is impossible to extract the copper from sulfide ore with sulfuric acid alone. Ferric sulfate is helpful for this purpose, provided the crude ore contains no alkaline earth to precipitate the iron before the solvent action of the ferric sulfate can become effective; but in the weathering process of porphyry ores there is nearly always some free base material of this character.

With both soluble oxide of iron and residual sulfide minerals present in the ore, the question arises whether it might not be better to strike at the root of the trouble and roast the crude ore before leaching in order to make the iron oxide less soluble and to make the copper, as sulfide; soluble. I will admit that, at first sight, a roasting plant of this magnitude might appear to be a prohibitive expense; but when the expense of a leaching and electrolytic plant is considered, such as that constructed at Ajo, which is replaced in a few years by a proportionately expensive concentration plant to treat the sulfide ores, the expense in the first place of a roasting plant that would assure the continued use of the leaching plant for the sulfide ores, might not be a bad investment when the final balance sheet is made. Anaconda has sufficiently demonstrated that roasting low-grade material for leaching is not impracticable. On the other hand, a concentration and flotation plant might be installed in the first place for the treatment of both oxidized and sulfide ores and this augmented by a roasting and leaching plant. Should the latter suggestion be adopted, it would be a small matter to go a step further and add chloridizing roasting to the flow sheet, thereby securing the economic advantage of the chlorides of copper for electrolytic precipitation. This would also avoid any loss from undecomposed sulfide of copper that might occur from desulfurizing roasting alone. This process has been successfully operated in Europe, since 1860, on pyritic cinder containing less than 3 per cent. copper and has been used in this country for a long time. Such a process would not be commercial on porphyry ores carrying  $1\frac{1}{2}$  per cent. copper, but it has possibilities worth considering. Salt is a cheap reagent and is cheaply transported.

COLIN G. FINE, \* New York, N. Y.—On p. 566, the author says; "It is possible, by this process, to deposit about 50 per cent. more copper per kilowatt-hour than that shown by the published accounts of the large electrolytic copper extraction plants now in operation;" and on p. 551, "Inasmuch as 50 per cent. of the power for deposition could be saved by the successful use of carbon anodes, it might be well to give carbon a trial under the new conditions." This 50 per cent., according to our experience, seems very high as compared with our values for the chilex copper silicide anode. We would be interested to obtain further details

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of the conditions under which this high value of 50 per cent. was obtained.

ARTHUR L. WALKER,\* New York, N. Y.—Is that not due to the difference in the salt?

EDWARD F. KERN,† New York, N. Y.—The low-power required is probably due to the use of carbon anodes, and  $\text{SO}_2$  depolarizer, which brings about the low potential drop; that is what he has reference to. By using carbon anodes, it is possible to produce sulfuric acids by oxidation of  $\text{SO}_2$ , and the heat of formation of the sulfuric acid causes a corresponding reduction of power. This has been shown in the laboratory, whether the  $\text{SO}_2$  is added through the perforated anodes or added directly to electrolyte alone.

R. C. CANBY, Wallingford, Conn.—But you would not get 50 per cent. I have seen 50 per cent. given somewhere in literature on this subject, but I cannot recall where; he may have gotten it as an accepted fact.

HENRY A. TOBELMANN, Brooklyn, N. Y. (written discussion).—The process here described is very similar, in many respects, to the process so successfully used in treating about 10,000,000 tons of oxidized copper ores by the New Cornelia Copper Co. at Ajo, Ariz. Up to 1912, there were no leaching plants in operation with tonnages sufficient to create much interest, with the possible exception of Rio Tinto, where heap leaching had been carried on for a long time. About this time, however, the experimental work carried on, under the supervision of E. A. Cappelen Smith, for the beneficiation of the Chuquicamata ore had been brought to a close. Van Arsdales and Addicks were still carrying on leaching tests in Douglas, and work on the New Cornelia problems was under way.

The Ajo work was carried on first with the idea of simple sulfuric-acid leaching followed by precipitation on some form of iron. The use of iron suggested metallizing the acid-plant calcines and using the resulting sponge iron. In the fall of 1913, the management became interested in the possible application of electrolysis, as there seemed to be no reason why standard refinery practice should not be applied to the solution of this problem. A process using a patent wood-veneer diaphragm anode, (invented by F. L. Antisell) was tried. The process consisted of: (1) Leaching with sulfuric acid by upward percolation, (2) reduction of the ferric sulfate in the pregnant solution with sulfur dioxide, (3) maintaining separate circulation of the anolyte and catholyte, (4) return of the anolyte to the ore. The difficulty of maintaining this separate

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circulation of anolyte and catholyte and the bulkiness of the patent anode made a large installation of this process impracticable. The three months' work, however, showed a few of the advantages of upward percolation and sulfur-dioxide reduction. During this work, towers filled with coke were first tried; later, this coke was replaced with quartz. Gas scrubbers were then suggested; first a vertical and later a horizontal cylindrical scrubber was tried. The latter form was similar to that now employed by the author. While the results were much alike, it was agreed that towers would be less expensive to build, less troublesome to operate, and less difficult to keep clean.

The author reduces the ferric sulfate as fast as it is formed by circulating his electrolyte in closed circuit with his reducing apparatus. At Ajo, the solution is reduced but once per cycle. Continuous reduction was, at one time, considered but early in our work we found that the difficulty of reducing ferric sulfate with sulfur dioxide increased as the acid increased, and that while a neutral solution was quite readily reduced, an acid solution was not. The author's successful solution of this problem is of great importance as continual reduction of the ferric iron will mean improved ampere efficiency.

The author uses hydrogen sulfide for the precipitation of the copper from the discard solution; at Ajo scrap iron is used. He dissolves the copper sulfide in tank-house electrolyte, taking advantage of the beneficial reducing action so obtained; at Ajo, a part of the process consists of dissolving the cement copper in a similar manner and with the same purpose in view. It was our opinion that the use of hydrogen sulfide for this precipitation was more expensive than the use of scrap iron for this purpose. Probably many of the former disagreeable features of the use of this gas have been overcome by the author.

The production of acid by the Greenawalt process is important, as it makes the process not only self-contained but independent of outside conditions. At Ajo, we were able for quite long periods to carry on leaching with the addition of but a small quantity of outside acid. Under normal conditions, probably 70-75 per cent. of the total acid neutralized per ton of ore in the plant of the new Cornelia Copper Co. is plant acid.

In this connection, a few words regarding acid concentration might be of interest. In the leaching of copper ores with sulfuric acid, the acid concentration is very important. Sulfuric acid has a selective action for copper, while the lower the acid concentration the longer is the time of leaching necessary; on the other hand, the less impurities will be dissolved per pound of copper. This fact was brought most forcibly to our attention during 1921 when, as a result of the unusual condition of the copper market, we were allowed to operate at 50 per cent. capacity. To operate the plant to the best advantage, this meant leaching 16 days as against the normal period of 8 days, and resulted in leaching with

1.2 per cent. sulfuric acid against the normal of about 2.4 per cent. Comparing the results for 1920, a normal year, with those of 1921, when operating at 50 per cent. capacity, showed that in the former case about 40 to 50 per cent. of the acid was neutralized by impurities as against 10 to 15 per cent. in the latter case.

The author states that a solution low in iron will act more energetically on the iron in the ore than a solution high in iron. While this may be so, our experience at Ajo does not entirely agree with it. The principal impurity dissolved at Ajo was not iron but alumina. Of the total acid combined with impurities, approximately 52 per cent. was combined with alumina, 32 per cent. with iron, 15 per cent. with magnesia, and 1 per cent. with lime. The greater the acid concentration, the greater is the acid consumption per pound of copper leached, and it will be quite necessary to determine the most profitable acid concentration for each ore to be treated.

On p. 532, the author speaks of the necessity of the neutralization of the free acid before the precipitation of the copper by iron can be accomplished. I believe that in refinery practice copper solutions are precipitated by means of iron which contains as much as 15 per cent. free sulfuric acid. Complete precipitation is generally obtained without neutralization and without excessive iron consumption.

On p. 533, he says, "all things considered, the electrolytic method can stand a fairly high power cost . . . of 1 cent per kw.-hr. I am of the opinion that neither at the Chile Copper Co. nor at the New Cornelia Copper Co. is the cost of power less than this figure. It might also be of interest to know that the power cost is approximately half of the total electrolytic cost.

On p. 563, the author says that copper can be deposited out to as low as 0.25-0.50 per cent. We found that when the copper in our solutions at Ajo reached 1.0 per cent. the deposit became brittle; when the solution reached 0.5 per cent. the deposit was mossy and would fall off in masses similar to cement copper. The results obtained by the author are probably the result of the high acidity and the sulfuric dioxide in the solution.

Much stress was laid on the necessity of having a roaster gas high in sulfur dioxide; it was said that such a gas could be obtained only by burning elemental sulfur. Quotations on elemental sulfur were obtained and plans made to burn 20 tons or more per day. On investigating the work that had been done at paper mills, we found that by roasting pyrite under proper conditions, there could be obtained a gas nearly as high in sulfur dioxide as when elemental sulfur was burned. As a result, instead of buying elemental sulfur at \$30 per ton, we were able to use Bisbee pyrite, which cost less than half as much and of which we had a great quantity. For a while we were somewhat perturbed about the



strength of gas necessary. Like many other things the importance of this had been exaggerated; excellent reduction has been obtained with gas containing as little as 3 per cent. sulfur dioxide. This does not change the fact, however, that the more concentrated the gas the more active will be the reaction.

On p. 562, the author states that to dissolve a 15 per cent. concentrate it would be necessary to circulate the solution between the leaching tanks and electrolytic tank house about thirty times. I do not think that the conditions of treating an ore carrying 15 per cent. copper with those existing when treating a 1.5 per cent. copper are comparable. To begin with, a 3-mesh 15-per cent. ore would never be treated by leaching. The acid concentration also would be quite different, being nearer 10 per cent. than 2.5 per cent. I can, however, readily visualize the treatment of a 15-per cent. ore without much difficulty.

On p. 541, the author states that absorption towers used for reducing ferric iron in copper solution have not given as good results as were hoped for even with the use of towers in series. The towers at Ajo are the only ones I know of used for this purpose and they have done what we expected of them. In this connection, I would be much interested to know the space required by the special device to reduce a quantity of ferric sulfate equal to that treated per day at Ajo.

In considering the ferric-sulfate results given as representative of operations at Ajo, it should not be forgotten that as time went on conditions improved to such an extent that the ferric sulfate in the solutions entering the tank house probably averaged not over 0.05 per cent. for the last five years of operation, and those leaving the tank house probably not over 0.40 per cent. For the past three years, these figures will probably average about 0.05 per cent. in and not over 0.30 per cent. out of tank house.

OLIVER C. RALSTON,\* Berkeley, Calif. (written discussion).—The reduction of ferric-sulfate solutions by sulfur dioxide is discussed, on pp. 540-543, especially in connection with the reducing towers of the New Cornelia Copper Co., at Ajo. In roasting ore and passing the roaster gases into the reducing towers, the Ajo plant is actually passing more oxygen than sulfur dioxide through their solutions. Normally, as pointed out at the bottom of p. 563, oxygen from the air is quite inert toward either sulfur dioxide or ferrous-salt solutions at the temperatures involved. However, the Bureau of Mines has, for several years, been studying the simultaneous oxidation of sulfur-dioxide and ferrous-sulfate solutions by air and finds that it is quite rapid. The two reducing agents together are quite easily oxidized by air and the reactions are spoken of as being "induced reactions." One reducing agent acts as a "promoter"

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\* Superintendent Pacific Experiment Station of Bureau of Mines.

and the other reducing agent acts as an "accepter." Possibly the sulfurous acid takes up an oxygen molecule to form monopersulfuric acid,  $\text{H}_2\text{SO}_5$ , which is unstable and gives up an oxygen atom to the ferrous sulfate, which can thereby be oxidized to the ferric state. Alternatively, the ferrous compound may be the first to promote the reaction by taking up the oxygen molecule to form a peroxidized iron salt, which then loses part of its oxygen to the sulfurous acid in solution, making it become sulfuric acid. Whether the ferrous iron or the sulfurous acid is the acceptor is unimportant to the metallurgist. The fact remains that the simultaneous rapid oxidation of the two reducers is possible and seems to be of possible commercial value. This explains the difficulty that has been experienced at Ajo in reducing the solutions. Fortunately, a tower is one form of apparatus in which reduction can be accomplished more rapidly than oxidation by the air takes place; but complete reduction is impossible. Our experience is counter to the surmise of the author, on p. 543, that a finer division of the gas current or of the solution would aid reduction. We find that the greater the surface of contact the more efficient is the oxidation reaction. If the gases are passed through the iron-sulfate solutions in fine bubbles, as in a flotation cell, the oxidation reaction preponderates; and with sufficiently fine bubbles the same gas that reduces at Ajo in the present towers would almost completely oxidize ferrous iron to the ferric state. The form of the apparatus is, therefore, of extreme importance.

We find that increasing acidity of the solution decreases the rate of the oxidation, just as the Ajo plant and the author finds that acidity decreases the reduction rate. We have utilized this fact in working out an analytical method for determining sulfurous acid and ferric iron in the presence of each other—we strongly acidify the solution to stop reduction of the ferrous iron by sulfur dioxide and immediately titrate the ferrous iron and subtract from the total iron analysis to determine the ferric iron present.

On pp. 550 and 559, the author says that the ferric sulfate which he cannot reduce by roaster gases to the ferric state may also be inactive with respect to the copper cathodes in an electrolytic cell. This discussion of the reason for this "unreducible" ferric iron will make it clear that its failure to reduce by the roaster gas in the tower has nothing to do with its ability to be reduced by metallic copper in the deoxidized solutions adjacent to the cathodes. All that is necessary is to keep atmospheric oxygen away if the ferric iron is to be completely reduced. By using pure sulfur dioxide and keeping out oxygen entirely, a complete reduction would have been possible.

The Greenawalt reduction step by sulfur dioxide is limited to solutions of low acidity and to the use of gases containing high sulfur dioxide content and low oxygen content. When roaster gases are used, fine

division of the gas, as obtained in the more efficient absorbers, is to be avoided.

This brings up the question as to whether two-stage reduction is necessary at all. Hydrogen sulfide, as used by the author for making precipitated copper sulfide, which will perform the second step of reduction, is at best an expensive and dangerous gas to handle. Besides it is interesting to note, on pp. 558 and 559, that when agitating some of the partly reduced solution with copper sulfide precipitate by means of compressed air it was impossible to obtain a complete reduction, even with excess copper sulfide, and 0.11 per cent. of "unreducible" ferric iron remained in the solution. Evidently another induced reaction involving solid copper sulfide and ferrous sulfate solutions, with air as the oxidizer, is involved. Again let me object to the author's surmise that the "unreducible" ferric iron will be indifferent toward the copper cathodes in the electrolytic tanks.

On p. 560 is a summary of Demonstration Test B in which an electric current efficiency of 106.9 per cent. was obtained during part 2. The author explains this as due to the presence of cuprous chloride in the solution. As cuprous chloride is not very soluble I suspected that, like the New Cornelia plant cathodes, the cuprous chloride would be found in part in the cathodes themselves and that they were therefore too heavy by at least this amount. I therefore called at the plant where this work had been done and obtained the chlorine analysis of the cathodes, which was 0.45 per cent. for all the cathodes produced during the period of experimentation. Unfortunately the chlorine analysis of the cathodes from this particular test was not available. However, this corresponds to 1.26 per cent. anhydrous cuprous chloride in the cathodes, with a good possibility that the particular batch in question had been more highly contaminated. The only comment that can be made safely, therefore, is that the current efficiencies reported are probably too high and an apparent efficiency of 106.9 per cent. may not be due to the electrolysis of cuprous chloride but to chemical deposition of cuprous chloride on the cathodes, in whole or in part. I state this to emphasize the author's acknowledgment of the condition.

The author has summarized quite well the advantages of making electrolytic copper direct from the ore and his process is his solution of the vexing problem of what to do with the impurities in the electrolyte. I wish, however, to discuss the advantages of having a little ferric iron in the solutions instead of eliminating it as the author does. In the first place, it attacks sulfides in the ore. During a visit to the Ajo plant some time back, I found that about 40 per cent. of the sulfide copper present in the oxidized ore was being recovered through its dissolution by means of ferric iron in the solution from the electrolytic cells. Also, H. W. Morse (in a private communication) said that with solutions completely free

of iron he found it difficult to get firm smooth cathodes; seemingly a small amount of ferric iron is wanted.

Even such a plant as that of the New Cornelia does not make finished copper, as the cathodes contain enough chlorine to make melting necessary in order to slag it. Cement copper can be made well over 90 per cent. pure, as exemplified by the recent work of the Ohio Copper Co., and likewise will be melted in the refining furnace and most of its impurities removed before casting. If a little trouble is taken in purifying solutions before cement copper is made, so that the cement can be sold direct to the remelting furnace of the copper refinery, a much less expensive plant than an electrolytic leaching plant can be built.

WILLIAM E. GREENAWALT (author's reply to discussion).—Since the paper was written, the process has been tried in a small complete demonstration plant. These tests show that 1.4 lb. of copper can be deposited per kilowatt-hour in the regular operation of the process, using lead anodes. This result is probably due to the high ampere efficiency obtainable under effective reduction of the ferric iron, to the higher permissible temperature, and to the increased acid and salt content of the electrolyte.

By the use of carbon anodes, the voltage required for the deposition of the copper is greatly reduced. The obstacle to the use of carbon anodes in sulfate solutions, however, has been the disintegration of the carbon, but this obstacle is not considered insurmountable. Anson G. Betts was one of the first to call attention to the possibility of carbon anodes in the electrolysis of sulfate solutions containing ferrous sulfate, and in 1905 patented the process of moving carbon anodes through the solution to facilitate depolarization. He claimed reasonable permanence for the anodes and an increased current efficiency of from 50 to 100 per cent. He also called attention to the advantages of high temperature in effective depolarization in the use of carbon anodes without moving the anodes.

In 1915, Addicks, after careful experiments with carbon anodes in electrolyzing copper-sulfate solutions containing ferrous sulfate, came to the conclusion that "carbon anodes will stand up in sulfate liquors if they are properly depolarized," and that, "2.25 lb. of copper per kilowatt-hour can be recovered under proper operating conditions." It is therefore thought that 1.4 lb. of copper per kilowatt-hour, direct current, using lead anodes, is about 50 per cent. more than that given in published accounts; and that 2.25 lb. per kilowatt-hour, using graphite anodes, would increase this from 50 to 100 per cent. If chloride solutions are used, it may be possible even to double the latter figure.

As the process described is in no way limited to the use of any particular anode, possibly copper-silicide anodes may show an increased efficiency over lead anodes, as they have at Chuquicamata, should copper-silicide anodes become generally available. It is believed, however, that if

conditions can be arranged to prevent the unusual disintegration of carbon anodes, no metal anodes will be able to compare with them in point of current efficiency.

In 1911, the author made an estimate for George H. Augustine, President of the Cornelia Copper Co. (old) for a 1000-ton plant based on sulfate leaching, electrolysis, and sulfur-dioxide reduction in towers. He had been experimenting with two towers 30 ft. high, one filled with coke, the other with pebbles. The coke tower seemed to give the best results.

The limitations of such a process were evident to the author at the time, as has since been found at the New Cornelia, and his ideas were fairly well advanced to overcome the difficulties, but it is a far cry from an idea to a process. Nevertheless, with all the imperfections of so crude an electrolytic process, he was firmly convinced, when he made the estimate for Mr. Augustine, that it was far in advance of any purely chemical method available at that time. The remarkable achievements at the New Cornelia with the electrolytic process there in use are due more to the superior engineering and metallurgical talent employed in developing the process, than to any intrinsic merit the process itself may possess.

The cost of chemicals, or material, per pound of copper precipitated from waste or foul solutions, is about the same when using hydrogen sulfide as when using iron. By the use of hydrogen sulfide, the amount of copper to be precipitated is relatively small as compared with iron precipitation, and the precipitate is much more cheaply handled. Careful tests in a small demonstration plant showed that the copper could be deposited electrolytically from waste solutions to as low as 0.10 per cent., from a head electrolyte containing 4.0 per cent. copper, used cyclically in the process. To state the matter differently, the comparison should be made between precipitating 0.10 per cent. copper from the waste solutions with hydrogen sulfide, as preferred in the Greenawalt process, and the 2.12 per cent. given for the New Cornelia; much less copper solution would be wasted in the Greenawalt process than at the New Cornelia for the regular solution can be electrolyzed with a higher iron and acid content.

A high-acid solution will dissolve more iron and other impurities than a low-acid solution, under the conditions at the New Cornelia; that is, with the solution in contact with the ore for 8 days under normal conditions and 16 days under very low acid conditions, but this does not apply generally. In other words, the solution of impurities is mostly a function of time as well as of acidity, and if the strong acid solution is in contact with the ore a short time the amount of impurities dissolved probably will not be much larger than if a weak acid solution is in contact with the ore a long time, the copper extraction in both cases being the same. In

treating copper ores, the author prefers agitation to percolation, using fairly strong acid solutions, with the time element reduced to a minimum. With weak solutions, the time element is too great for satisfactory use in agitation. A satisfactory extraction can be obtained on many ores with a few hours agitation. It is probable that agitation would necessitate finer grinding, but finer dry grinding in large rod mills, while not as cheap as wet grinding, is quite within the range of practicability and screening, with dry rod-mill grinding, could be dispensed with, or greatly reduced.

Alumina, to a certain point, is beneficial in the electrolyte, and no particular attention need be given it in the deposition of the copper. Its principal detrimental effect would probably be in the leaching, but this is not so pronounced with agitation as with percolation.

It is well known that copper can be effectively precipitated from acid solutions with iron, without neutralizing the acid, but it is doubtful whether the copper precipitation can be made complete, or almost complete, without first neutralizing, or nearly neutralizing, both the acid and the ferric iron. At the New Cornelia, both the acid and the ferric iron are practically neutralized to get the copper content in the effluent down to 0.02 per cent.

Copper deposited from a 4.0 per cent. solution down to about 1.0 per cent. gives bright cathodes of high purity. At about 1.0 per cent., the solution, diluted with a certain amount of water, is returned to the ore. The relatively small discarded portion is electrolyzed from 1.0 per cent. down to about 0.10 per cent. In depositing from 1.0 per cent. down to 0.5 per cent., the cathodes are firm and fairly pure. At about 0.5 per cent., they show discoloration; and at 0.10 per cent. the deposit becomes granular, rather impure, and may drop from the cathodes. The copper from this portion of the electrolysis contains from 84.5 to 98.5 per cent. copper, the principal impurity being oxygen; the copper is deposited at the rate of about 0.75 lb. per kw.-hr. This copper would probably be pure enough for direct fusion refining, or it could be redissolved and converted into pure cathodes.

In the use of towers, the experiments at Ajo showed what the author had found in his experimental work; viz., that as the acidity of the electrolyte increases the reduction of the ferric salts becomes more difficult. At Ajo, the reduction in towers, with sulfur dioxide, was so unsatisfactory that apparently no serious attempt was made to surmount the difficulty of reduction with acid solutions. The process, as there adopted and patented, was based on the idea of maintaining a substantially neutral solution for effective reduction. It is at this point that some of the author's work diverges radically from that done at the New Cornelia; he worked along the lines of reducing acid solutions, which at the New Cornelia was thought to be impractical.

While more reducer space will be required in the Greenawalt process than tower space at the New Cornelia, reducer space, or volume, is cheaper to install than tower space; and when the storage tanks and spraying chambers at the New Cornelia are taken into consideration the difference will not be so great as to be objectionable.

The economy of the Greenawalt process has not been fully developed, but it is thought that a comparison of the first results obtained under demonstration conditions could be fairly compared with the results of the first two years of operation at the New Cornelia, as published. However, the figures given for the reduction of the ferric iron at the New Cornelia for the past three years are not fairly comparable with those given for the Greenawalt process, as the reduction at the New Cornelia includes the use of cement copper (presumably about 25 per cent. of the total amount of copper produced) which is redissolved in the electrolyte with the simultaneous reduction of ferric iron, while the figures given for the Greenawalt process are based on the use of sulfur dioxide alone, unless otherwise stated.

It is not thought that the finer division of the liquid in the gas, in the Greenawalt reducers, necessarily acts more energetically than in towers, and no essential step of the process is based on that distinction. The advantage is based more, primarily, on the application of the gas to large volumes of the solution and at a higher temperature, thus emphasizing the elements of time and rapidity of reaction. With neutral solutions, the ordinary reducing reaction between ferric iron and sulfur dioxide offers no particular difficulty. The difficulty increases with the acidity, and the acidity increases proportionately to the copper deposited. In the Greenawalt reducers, a large volume of the solution is under continuous treatment with the gas, practically under conditions of saturation; while in towers, the treatment is of relatively short duration.

The process is not sensitive, either as to the concentration of the gas or the acidity of the solution, within the limits of practical leaching operations, or say up to 8.0 or 10.0 per cent. acid. In very complete tests recently made, the sulfur dioxide in the gas used did not exceed 2.0 per cent., most of the time it was less; 1.4 lb. of copper was deposited per kilowatt-hour under these conditions, depleting the copper in the solution from 4.0 to 1.0 per cent., when it was returned to the ore. The deposited copper was of high purity.

The reference to the oxidation, instead of reduction, of the soluble iron, when treated with sulfur dioxide, is interesting. For years the author has been familiar with the patent to Deby,<sup>14</sup> in which is claimed "The method of regenerating the iron sulfate used in lixiviation, which consists in subjecting the ferrous-sulfate solution to the fumes or gases of

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<sup>14</sup>Pat. No. 240309, April 19, 1881.

sulfurous acid, whereby its conversion into ferric sulfate is effected." Ordinary towers are mentioned as suitable apparatus to carry out the process. The reaction, under the conditions under which the author was operating, was always reducing. When 2.0 per cent. gas was used, it was passed through four small reducers in series. It is realized that a highly concentrated gas, say gas containing 7.0 to 9.0 per cent.  $\text{SO}_2$ , with a consequent minimum oxygen content, would be much more effective than a gas low in  $\text{SO}_2$ , with a corresponding relatively high oxygen content, but a process to be practical cannot have very narrow limitations.

It is realized that the "unreducible" ferric iron from  $\text{SO}_2$  or  $\text{CuS}$  reduction is attacked by metallic copper, but his experience leads the author to conclude that it would be more or less with the same difficulty as further attack with  $\text{SO}_2$  or  $\text{CuS}$ . Complete reduction in a commercial plant is very difficult under any condition.

When copper is deposited from a chloride solution, or a solution containing chlorine, it is rarely, if ever, free from chlorine; with 0.45 per cent., or more, chlorine in the cathodes, this would not account for much of the excessive current efficiency of 106.9 per cent., in test B; whereas, the deposition from the cuprous chloride would account for it, allowing for the relatively small amount of the chlorine as an impurity.

Two-stage reduction is not necessary: in fact in the tests given in the paper, and in much more careful and elaborate tests recently made, practically all the reducing was done with sulfur dioxide. In the first tests the copper sulfide was applied to the waste solutions from sulfur-dioxide reduction; and in the later tests the copper sulfide was applied direct to the leach solution without any application of sulfur dioxide. The cathodes obtained in the later test, with  $\text{CuS}$  reduction alone, were bright and of exceptional purity, and the electrolysis showed no signs of weakness until the  $\text{CuS}$  was practically exhausted and the copper in the electrolyte depleted to 0.62 per cent., with an acid content of 6.20 per cent. The average ferric iron in the reduced solution was 0.051 per cent., and 1.4 lb. of copper was deposited per kilowatt-hour, direct current, for the entire test.

Manifestly, if ferric iron is desired in the leach solution, it can be increased to any extent desired, as at the New Cornelia, by bypassing the solution around the reducer, or by simply circulating the solution through the last group of cells and diverting a portion of the effluent solution from the cells to the leaching department and another portion back to the reducer. In any event, it is not intended to reduce the electrolyzed solution from the last group of cells before returning it to the ore, and the operator can determine the ferric content desired.

It is true that very pure cement copper can be made with a relatively pure iron and by purifying the solutions before precipitation. The 90



per cent. cement copper produced by the Ohio Copper Co. is of exceptional purity for cement copper, and the solutions are not purified, but the iron used is clean detinned scrap and is considerably more expensive than common scrap iron. As a matter of fact, common scrap iron is not a desirable precipitant; at the New Cornelia and at the Mountain Copper Co., scrap tin is principally used.

Electrolytic plants are expensive to install, compared with iron precipitation plants, but the electrolytic plants can be much more economically operated. The comparison cannot be limited to the cost of power and the cost of iron per pound of copper produced. Assuming a net consumption of about 3.0 lb. of acid per pound of copper produced, as in the New Cornelia experiments, the comparison should be made on the basis of 3.0 lb. of acid for solution and 1.0 lb. of iron for precipitation, as against 1.4 lb. of copper per kilowatt-hour, direct current, with the simultaneous regeneration of about 3.0 lb. of acid, which is used to dissolve the copper. If an acid plant is installed in connection with iron precipitation, it will cost nearly as much as an electrolytic plant; if the acid is bought and shipped in, the cost of the acid in most cases will be prohibitive, and if the mine is not located on a railroad, as is usually the case in new or small developments, the importation of acid cannot be even considered.

Much has been said about the danger or inconvenience of handling hydrogen sulfide on account of the poisonous nature of the gas. The author has had fairly wide experience in the use of hydrogen sulfide and cannot agree with this opinion. He was for some time foreman and also research metallurgist in one of the largest chlorination mills in the west, where about 500 tons of gold solution were precipitated daily with hydrogen sulfide, but he does not recall an accident or even a serious inconvenience resulting from the use of hydrogen sulfide in that plant, notwithstanding that the generator was located in the barrel room and the precipitation tanks were in the same room with the pressure tanks and filter presses, where the solutions were filtered. In a small plant recently erected for demonstration purposes in connection with the Greenawalt process, four sulfur-dioxide reducers, one hydrogen-sulfide generator, the hydrogen-sulfide precipitator, the  $\text{CuS}$  reducer, electrolytic tanks, pumps, motor-generator set, etc., were located in a small building of but one room, and although the work was practically under continuous operation for three months, there was no occasion to call in the first-aid department, and no complaint was made of escaping hydrogen-sulfide gas, although the plant was located in a small city. The fact is that the gas is easily controlled, and any one familiar with the handling of corrosive gases should not have the slightest difficulty in designing a plant as safe and as free from objectionable features as any other chemical plant, and certainly as safe, comfortable, and sanitary as a smelter or a cyanide plant.

## Direct Electrolysis of Black-copper Anodes of High Nickel-lead Content

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(New York Meeting, February, 1924)

SOME years ago, at the plant of the Baltimore Copper Smelting & Rolling Co., the receipt of large quantities of copper blister running high in lead, nickel, and arsenic resulted in the formation of a great amount of very foul slag, in the anode furnaces. A typical analysis of this slag was:

Gold, oz. per ton.....	0.09	Arsenic, per cent.....	0.60
Silver, oz. per ton . . . .	13.20	Antimony, per cent. . . .	0.50
Copper, per cent.. . . .	19.50	Silica, per cent.... . . .	28.30
Lead, per cent..... . . .	11.90	FeO, per cent... . . . .	19.20
Nickel, per cent... . . . .	4.60	CaO, per cent..... . . .	1.60

The problem was to get out the copper in marketable form, to save the gold, silver, and particularly the nickel, and to get rid of as much as possible of the lead, arsenic, and other elements that were valueless to the Baltimore plant.

In a copper refinery that does not take custom material for matte smelting, the usual method is to smelt the anode slag with coke in a reducing furnace, the black copper thus formed being sent back to the anode furnaces; this was the custom at Baltimore. An average anode slag will contain, perhaps, 40 per cent. copper and such small quantities of lead, nickel, etc., that smelting will get rid of most of these impurities in the black-copper furnace slag. To treat such an impure slag in this way, however, would result in a large nickel loss, and would send back to the anode furnaces all the lead and nickel not so lost, where it would be slagged off again and returned to the black-copper furnace as a slag still more concentrated in impurities. The result would probably be a constantly increasing amount of anode slag containing a likewise constantly increasing percentage of impurities. To avoid such a disastrous closed circuit some other process had to be devised.

A small multiple-tank room, built for impure copper as an adjunct to the main series electrolytic refinery, was available, so the following standard process was suggested:

1. Smelt, removing the earthy constituents and as much lead, arsenic, iron, etc., as possible.

2. Cast the product, which is very impure and high in nickel, into anode form.

3. Electrolyze direct by the multiple system, producing cathodes of marketable purity. Gold, silver, antimony, lead, and some arsenic should slime off, while the rest of the arsenic, together with the nickel, should go into electrolyte, which the Baltimore plant was equipped to treat, producing therefrom pure metallic nickel.

It was decided to ascertain experimentally whether such a standard process was metallurgically and economically sound.

### EXPERIMENTAL SMELTING

Several test runs were made in a small, round, water-jacketed cupola, both black-copper and matte smelting being tried. Matte smelting, however, was given up because even with a matte as low in grade as 45 per cent. copper, considerable very foul metallic copper, called "bottom," was formed. In addition, it would have been necessary to buy sulfur for making the matte, making the cost prohibitive. By running the percentage of coke in black-copper smelting up to about 20 per cent., and keeping the slag-fall as low as possible, over 80 per cent. of the nickel could be retained in the black copper formed, whereas almost 75 per cent. of the lead could be driven off as fume or gotten into the slag; also from 35 to 45 per cent. of the arsenic was eliminated. It was particularly desirable to eliminate lead and arsenic, so that, from a strictly copper-refining point of view, these results were quite satisfactory and the test runs were concluded pending determination of the feasibility of direct electrolysis.

### EXPERIMENTAL ELECTROLYSIS

A few hundred pounds of the very impure copper produced in test runs were cast into the shape of Wohlwill gold anodes, which were subjected to experimental direct electrolysis with the following objects in view:

1. To find what quality of cathode copper would be obtained.
2. To ascertain the analysis of the slimes obtained.
3. It was hoped that all the nickel would go into the electrolyte and most of the arsenic into the slimes. It was thought, however, that considerable nickel would be present in some insoluble form, such as an arsenide or antimonide, and hence would slime with the other metals, in which case direct electrolysis would be of no use as far as nickel recovery was concerned.
4. The removal of electrolyte from the series-tank room for purification had always been effected through the multiple-tank house circulation,

into which series electrolyte was daily drawn off. Fouler multiple electrolyte was then drawn off to insoluble anode tanks, which removed the copper preparatory to delivering it to the nickel plant for nickel recovery. If impure anodes running high in nickel could be electrolyzed direct in the multiple-tank room circulation, it was thought that the multiple electrolyte could be largely enriched in nickel and depleted in copper before going to the depositing out tanks referred to, thus effecting a saving in power there and increasing the nickel concentration of the solution sent to the nickel plant, thereby cutting costs in that department.

The experimental work was carried on in small tanks, of the size ordinarily used in gold electrolysis by the Wohlwill system. The anodes were  $7\frac{1}{2}$  by 4 by  $\frac{5}{8}$  in. The current density was 18 amp. per sq. ft. The composition of anodes actually used was:

Gold, oz. per ton....	0 35	Nickel, per cent.....	11.0
Silver, oz. per ton ...	51 70	Arsenic, per cent.....	1.5
Copper, per cent .....	70.0	Antimony, per cent. ....	1.8
Lead, per cent.. ...	10.7		

The electrolyte was made up of regular tank-house electrolyte and was kept at an average temperature of 125° F. Table 1 shows an average analysis and also the maximum and minimum percentage that any constituent reached (of course, all were not high or low at the same time; for example, nickel was lowest at the start and highest at the finish; the table shows the extent of variation).

TABLE 1.—*Analyses of Electrolyte in Experimental Work*

	AVERAGE ELECTROLYTE	HIGH ELECTROLYTE	LOW ELECTROLYTE
Specific gravity....	1.278	1.305	1.250
Free acid, per cent ...	12 18	12.65	11.95
Copper, per cent .....	2 86	3.33	2.56
Nickel, per cent.....	2 77	3.34	1.71
Arsenic, per cent.....	0.70	0.80	0.60
Chlorine, per cent.....	0.0053	0.0104	0.0014

The anodes dissolved very uniformly. A large quantity of slimes was formed, which adhered to the anodes and had to be scraped off at intervals. The slimes naturally caused polarization, the voltage at times building up to over 2 volts. Immediately after scraping off the slimes the voltage was about 0.3; the average for the entire run was 1.07 volts. At times, the voltage would stay low for a long period and at others it would reach the maximum in less than 15 min. Usually the voltage would remain low for about  $\frac{1}{2}$  hr. and then build up gradually to about 1.7 volts, where it would remain until the anodes were scraped.

The run lasted 191½ hr. The slimes were removed when the run was half finished as well as at the end. The electrolyte was rapidly depleted in copper and acid, so that bluestone and acid were added to keep it fairly constant. The quantities added were:

Copper added, per cent. of weight of anode.....	13 0
Acid added (total), per cent. of weight of anode..	25 0
Acid (free), per cent. of weight of anode...	5 0
Salt, per cent. of weight of anode...	0 05

A total of 21,800 gm. of anodes was electrolyzed, producing 18,225 gm. of cathodes and 8530 gm. of slimes, with a consumption of 17,349 amp.-hr. Ampere efficiency was accordingly about 89 per cent., and but 52 lb. of copper were deposited per kilowatt-day. The distance from anode to cathode was 1 in. It was expected that the average voltage would be considerably lower in a large tank than under the experimental conditions outlined, and that therefore the power consumed would be greatly lessened. The analysis of the slime was as follows:

Gold, oz. per ton.....	2.40	Arsenic, per cent.....	4.08
Silver, oz. per ton....	132.60	Antimony, per cent.....	5.49
Copper, per cent.....	21.79	Free acid.....	2.98
Lead, per cent.....	26.12	H <sub>2</sub> O.....	3.46
Nickel, per cent.....	1.97		

It was recognized that the disposal of slime of such a complex analysis would be troublesome for a copper refinery, but it was intended to leach out the copper as far as possible and then ship the residue to the lead refinery offering the best terms.

The cathodes produced were much purer than had been expected from such low-grade anodes, running over 99.85 per cent. copper with arsenic and antimony both below 0.0050 per cent., and lead, nickel and iron less than 0.04 per cent. Approximately 88 per cent. of the copper in the anodes went into the electrolyte to be deposited as cathode copper, the remaining 12 per cent. went into the slimes. Of the nickel, 93 per cent. went into the electrolyte, and only 7 per cent. into the slimes. All of the antimony was slimed. The analyses given would indicate that all of the arsenic also was slimed, but this is at variance with usual refinery practice and was not checked by the later tank-room work on a large scale. Of the cathode copper 74 per cent. was obtained from the anode, while 26 per cent. was deposited out of the electrolyte.

The experiment showed that the bulk of the nickel went directly into the electrolyte and away from the copper, silver, arsenic, lead, and other waste metals, instead of going into an insoluble slime with them as was feared, so it was decided to make several tons of full-sized anodes of similar, or even worse, analysis and hang these in the regular commercial multiple tanks.

## COMMERCIAL WORK

The cake molds upon the small casting wheel, into which black copper had been tapped, were replaced by standard size anode molds, roughly 36 by 36 in. No particular difficulty was encountered in casting the black copper in this form except the breaking of the lugs, the remedy for which is discussed later. Nor was there anything special about the smelting operation, as it consisted merely of the ordinary black-copper furnace procedure, except that slightly higher coke and lower slag fall were used to save nickel, and a slightly lower column to burn off lead. Purity of cast anodes was regulated by mixing ordinary casting-house slag in varying quantities with the very impure slag. Often the anodes would have a little white metal upon them; this was hammered off with chisels usually at small expense. It was hard to keep the anodes even in thickness, protuberances often being scattered over the surface, even though the mold wash had been carefully dried previous to casting.

In the original electrolytic work, only a few tanks of anodes were used; but as soon as it was found that no serious difficulties would be encountered, the number was gradually increased; the data here given refers to the practice adopted after perhaps 50 per cent. of the tanks were so filled. The tanks were 3 ft. 6 in. by 3 ft. 6 in. by 11 ft. 5 in. and at first 22 and 24 anodes were used to a tank; later, however, 26 anodes to a tank were used.

Anodes were carefully spaced with a light—that is, before solution was run into the tank an inspection light was lowered between the plates to make sure that they were hung in such a way as to give maximum ampere efficiency. Even under these conditions, the ampere efficiency was very low at the start because of the large lumps scattered over the surface of the anodes; in addition, many of the anodes were warped and out of plumb.

The main cause of low ampere efficiency, however, was the very bad contact between the anode lug and the triangular bar. At first, a few ampere efficiencies were below 60 per cent. and a very few were as high as 80 per cent., but as the difficulties were gradually eliminated the efficiency increased until it averaged about 84 per cent., with few individual sections under 80 per cent. and some sections 90 or 91 per cent. As 6250 amp. were passed through each tank, the current density was approximately 12.8 amp. per sq. ft. Anodes were cast about  $1\frac{3}{4}$  or  $1\frac{7}{8}$  in. thick, so that there was approximately  $4\frac{3}{4}$  in. from center to center of anodes, and  $1\frac{7}{16}$  in. from the face of the anode to the face of the cathode.

Electrolyte temperature was held between 120° and 135° F.; it would have been kept hotter if plant conditions had permitted. Circulation was at the rate of about 3 or 4 gal. per tank per minute. Incoming liquor was run in at the bottom of the tank and allowed to run off by gravity

from the top of the solution level in the tank at the other end, thus running counter to the natural gravity settling of the slimes. Electrolyte analyses varied, as shown in Table 2, which gives average analysis and also the maximum and minimum percentages that any constituent reached.

TABLE 2.—*Analyses of Electrolyte in Commercial Work*

	AVERAGE ELECTROLYTE	HIGH ELECTROLYTE	LOW ELECTROLYTE
Specific gravity.....	1.270	1.285	1.255
Free acid, per cent . . . . .	11.07	11.83	10.32
Copper, per cent.....	3.15	3.68	2.63
Nickel, per cent....	2.13	2.40	1.87
Arsenic, per cent.....	1.14	1.28	1.00
Chlorine, per cent....	0.00363	0.00457	0.00269

The rapid depletion of copper in the electrolyte was avoided by the constant addition of foul series electrolyte, rich in copper, and of impure bluestone and a copper-nickel sulfate purchased from another plant. Two drawings of cathodes were made from each batch of anodes, cathodes being pulled about every fourteen days whereas the anodes lasted twenty-eight days.

The slimes were very voluminous, so it was thought necessary to clean them out whenever cathodes were pulled instead of waiting for anode pullings, as in the case of the regular multiple anodes, because after fourteen days they had almost reached the bottom of the electrodes. On two or three occasions, however, it was impossible to clean the slimes when the cathodes were pulled, because of labor shortage or other plant operating condition, and to our surprise we found that although the slimes, after twenty-eight days, were perhaps 6 in. above the bottom of the cathode, the ampere efficiency was not appreciably lowered. Apparently the slimes were so foul and earthy as to be practically non-conductive and an insulator instead of a conductor, as in the case of normal slimes. Furthermore, these slimes did not seem to adhere to or be baked upon the cathodes; they could be easily washed off the smooth copper surface. As a result, thereafter, slimes were often allowed to go twenty-eight days without cleaning.

Actual daily glue and salt consumption were about 1200 gm. and 7000 gm., respectively, but it must be remembered that about 1200 cu. ft. per day of series electrolyte, carrying about 0.0006 per cent. chlorine, were added daily to but 20,000 cu. ft. of this multiple electrolyte, while 1200 cu. ft. of foul multiple electrolyte were run off daily for nickel treatment, so that there was a great wastage of chlorine and organic glue constituents over that which was actually consumed in affecting the physical properties of the cathodes.

The cathodes were remarkably smooth and tough, considering the impurity of the anode. This was probably the result of the low current density used. Typical analyses of cathodes from these tanks were as follows:

Silver, oz. per ton.....	1.0	1 11	0.95
Arsenic, per cent.....	0.0022	0.0032	Trace
Antimony, per cent.....	0.0027	0.0032	0.0010
Nickel, per cent.....	0.0030	0.0040	0.0030
Lead, per cent.....	None	None	None
Iron, per cent.....	0.045	0 063	0.058

The high iron content would prohibit the use of these cathodes for ordinary electrolytic shapes, but, at Baltimore, there was such a large proportion of very pure cathodes from the series and regular multiple systems that these few special cathodes were used in small proportions of total furnace charges without any difficulty. For this reason, no particular effort was made to increase the purity of the cathode product, but no doubt much better work in this respect could have been done had it been worth the extra cost necessary.

The voltage per tank varied widely. Like ampere efficiency it was very bad at the start, but gradually improved until a normal standard of perhaps 0.55 volt per tank was reached in which case about 95 lb. of cathode copper was deposited per kilowatt-day of power used.

The particular difficulties encountered were as follows:

*Polarization.*—Voltage on these special tanks was, of course, much higher than on the regular tanks, and unlike them, was not at all constant. If a tank were let alone it would start off with about 0.4 volt and build up slowly, but quite regularly, to perhaps 1.8 volts, as measured across the ends of the tank. This was caused by the accumulation upon the anode of insulating slimes too adherent to fall to the bottom of the tank, as in ordinary electrolytic refining. This difficulty was overcome by tapping the lugs of the anodes lightly with a small hammer. The inspection gang did this in addition to its regular ammeter work, so that the anodes were tapped about twice in each 8-hr. shift. The tapping usually reduced the voltage very quickly to 0.45 or 0.5 volt.

*High Contact Resistance.*—Contact between the anode lug and the triangular bar was very poor because of the low conductivity of the impure anode. In some cases the conductivity was so poor that the edge of the triangular bar was melted. The average contact voltage was well over 0.25, which is prohibitive for economical power costs, as well as rendering impossible any equality of distribution of current among the 26 anodes. This difficulty was remedied by placing in the anode mold flush with the underside of the long lug of the anode, just before the copper was poured, a strip of copper scrap about 7 in. long, 1 in. wide, and  $\frac{1}{4}$  in. thick, as



shown in Fig. 1. Copper was then poured in, and the two copper pieces became an integral part of the anode at the point where the anode would rest on the triangular bar in the tank room. As a result the contact voltage was reduced to about 0.04 and inspectors were able to keep the contacts shined up and equalized.

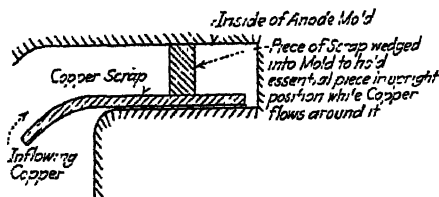


FIG. 1.

*Breaking of Anode Lugs.*—Many of the anodes were so foul that they did not look like copper, when struck with a hammer they would ring like a bell, and when broken would have an almost stony fracture. The lugs of such anodes frequently cracked in casting, and these lugs often were broken when the anodes were taken out of the molds or while handling them into the tanks. The tapping of the anodes also often broke an anode at the lug, letting the plate fall into the tank. As the anodes became old, many of them, no doubt as a result of the invisible cracks and checks formed during cooling in the molds, revealed weakness near the solution line at the lug and dropped into the electrolyte. This difficulty was partly overcome by inserting the two pieces of scrap into the anode, and was further obviated by placing additional longer pieces of copper scrap in the shoulder of the anode. It also was found advantageous to tilt the anode mold upon the ring in such a way that the anode was  $\frac{1}{4}$  in. or more thicker at the top than at the bottom, assuring a thick lug and shoulder.

The actual analysis of the anodes as charged varied very widely. The maximum and minimum of each constituent was:

	MAXIMUM	MINIMUM		MAXIMUM	MINIMUM
Copper, per cent.....	90.3	49.7	Antimony, per cent...	1.8	0.8
Lead, per cent....	18.6	3.8	Silver, oz. per ton.....	1270.0	9½
Nickel, per cent.....	21.2	3.4	Gold, oz. per ton.....	11.2	0.18
Arsenic, per cent.....	2.5	1.2			

A better idea of the actual contents of the anodes commercially treated is given by the average anode analysis; for the first month of running this was as follows:

Gold, oz. per ton.....	0.4	Nickel, per cent.....	12.4
Silver, oz. per ton.....	29.6	Arsenic, per cent....	2.50
Copper, per cent.....	66.2	Antimony, per cent.....	1.6
Lead, per cent.....	10.4		

For the succeeding three months of operation, the anodes ran:

Gold, oz. per ton.....	0.38	Nickel, per cent .....	9.9
Silver, oz. per ton ... ..	26.7	Arsenic, per cent . ....	2.2
Copper, per cent....	67.7	Antimony, per cent....	1.3
Lead, per cent.....	11.1		

For the next three months the analysis was as follows:

Gold, oz. per ton. ....	0.3	Nickel, per cent. ....	7.9
Silver, oz. per ton ...	22.2	Arsenic, per cent . . .	1.5
Copper, per cent. . . .	76.1	Antimony, per cent. . .	1.0
Lead, per cent....	7.3		

Grouping the first 1,250,000 lb. of anodes treated commercially, as to nickel content, the following rough divisions were obtained:

CLASS ANODES	POUNDS CHARGED
Nickel, over 14 per cent....	521,000
Nickel, 10 to 14 per cent.....	305,000
Nickel, 6 to 10 per cent.....	90,000
Nickel, under 6 per cent....	352,000
About 11 per cent average. ....	1,268,000

The percentage of scrap was very high at first, largely because of the number of anodes that dropped into the tanks by the breaking of the lugs. This percentage, for the first month, was 27.8; for the next three months, 19.4 per cent., and for the following three months, just about 20 per cent.

The quantitative metallurgical results were as follows: Of the copper in the anodes 9 per cent. went into slimes together with all the antimony, lead, silver, and gold, 46½ per cent. of the arsenic, and 5.6 per cent. of the nickel. The balance of the nickel and arsenic went directly into the electrolyte. About 20 per cent. of the total copper put into the form of cathodes was deposited from the electrolyte, the other 80 per cent. was from the anodes.

#### SLIMES

The slimes formed weighed, when dried, about 18 per cent. of the weight of anodes hung in the tank. Because of the irregularity in purity of anodes, the analyses of the slimes were subject to extreme variation, the gold running from 1.24 to 3.43 oz. per ton, the silver from 105 to 265 oz., the copper from 24 to 28 per cent., the lead from 23 to 29 per cent., the nickel from 1.43 to 1.7 per cent., the arsenic from 2.38 to 4.65 per cent., and the antimony from 3.56 to 6.93 per cent. The slimes produced in the first four months of operation were of the following average analysis:

Gold, oz. per ton....	2.16	Nickel, per cent.....	1.53
Silver, oz. per ton.....	168.0	Arsenic, per cent.....	3.3
Copper, per cent.....	26.0	Antimony, per cent.....	4.5
Lead, per cent.....	25.5		

Slimes from the next three months analyzed:

Gold, oz. per ton.....	1.74	Nickel, per cent.....	1 9
Silver, oz. per ton.....	126.6	Arsenic, per cent . . . . .	3 1
Copper, per cent . . . . .	28.2	Antimony, per cent. . . . .	3 4
Lead, per cent.....	22.6		

Our work on the treatment of this material was stopped when a buyer offered to take it without any further work upon it, paying for all silver, copper, and gold at a moderate treatment cost, but with no credit for lead; or expressing it in another way, paying for all gold, 95 per cent. of the silver, 95 per cent. of the copper, and about 68 per cent. of the lead at the same moderate treatment cost. This relieved us of the problem of slimes disposal, which threatened to be serious on account of the extremely low silver content of the slimes. The experimental work upon this problem had just started, but as an indication of what might be done it can be stated that two batches were roasted at low heat on a hearth and leached with spent electrolyte, such as was ordinarily used in the regular slimes treatment portion of the refinery. In one case 95 per cent. of the copper was extracted, and in the second case 83.6 per cent. In both cases, the weight of residue was just about half that of the original unleached slimes. The actual analysis of the leached slimes so produced was:

Copper, per cent.....	1.85	Arsenic, per cent.....	1.30
Lead, per cent. . . . .	52 72	Antimony, per cent.....	1.86
Nickel, per cent.....	0.22	Water soluble copper, per cent.....	0 47

indicating that a product running very high in lead, hence readily saleable to lead smelters under any market conditions, could be easily produced.

#### ADDITIONAL DEVELOPMENTS

A further development was the fact that the process outlined proved applicable to the treatment of speiss, which is always a bugbear in copper or lead work. An allied plant had large quantities of speiss analyzing as follows:

Gold, oz. per ton.....	1.90	Antimony, per cent.....	19.35
Silver, oz. per ton.....	16.40	Iron, per cent.....	0.83
Copper, per cent.....	6.44	Lime.....	Trace
Lead, per cent.....	0.94	Magnesium oxide. . . . .	None
Nickel, per cent . . . . .	38.67	Sulfur. . . . .	6.31
Arsenic, per cent. . . . .	22.39		

Another grade of speiss contained the following:

Gold, oz. per ton.....	0.60	Antimony, per cent.....	7.28
Silver, oz. per ton.....	45.60	Iron, per cent.....	0.65
Copper, per cent.....	24.27	Lime.....	Trace
Lead, per cent.....	24.40	Magnesium oxide.....	None
Nickel, per cent.....	16.02	Sulfur, per cent.....	3.89
Arsenic, per cent.....	18.07		

By adding this speiss to the black-copper charge, most of its constituents became a part of the multiple anodes cast therefrom, and experimentation revealed that the same separation of nickel from arsenic took place in the case of anodes from the speiss charge as from the regular impure anode slag charge without any speiss, so that the problem of getting the nickel in speiss away from the other components, especially arsenic, and freeing the silver and gold tied up, was readily solved. As in the case of the main problem, these facts were first determined experimentally in Wohlwill tanks, where it was found that of the arsenic in the anode about 41 per cent. went into the slimes, carrying 7 per cent. of nickel with it; the remaining 93 per cent. of nickel and 59 per cent. of arsenic went into the electrolyte, where arsenic was readily separated by the ordinary nickel purification methods.

### Costs

Direct electrolysis as above was more expensive than ordinary multiple-tank room refining in the following items:

Cleaning white metal from the face of cast anodes.

In general, wider spacing because of the lumps on the cast surface of the anodes. These apparently cannot be controlled, as in the case of ordinary anode casting. This wider spacing results in high power cost in the tank room.

High cost for the handling of the voluminous slimes and treatment of same.

Power costs all the way through would be much higher because of increased contact resistance and increased resistance in the lugs of the anodes, but especially because of polarization. Under these circumstances, much of this power cost was not chargeable to these impure anodes, but in any installation treating such material alone a very high power cost would have to be considered.

### CONCLUSIONS

Anode slag running only 20 per cent. copper, and containing over 10 per cent. lead and about 5 per cent. nickel was reduced in a black-copper furnace, and the very impure resulting material cast in anode molds.

These anodes, analyzing about 70 per cent. copper, 10 per cent. lead, 10 per cent. nickel, 2 per cent. arsenic, and  $1\frac{1}{2}$  per cent. antimony, were subjected to direct electrolysis by the multiple system at a current density of 12.8 amp. per square foot.

Fairly pure cathodes were obtained, the only abnormally high impurity being iron, which ran about 0.05 per cent.

About 94 per cent. of the nickel in the anodes, the equivalent of 75 per cent. of that in the original slag, was dissolved in the multiple electro-

lyte, from which it was readily recovered as nickel sulfate, which was later converted into pure metallic nickel.

About three quarters of the original lead was driven off in fume or slag during the smelting operation, the balance going into the slimes which, when leached, would contain nearly 50 per cent. of lead.

Operating difficulties, such as breaking of anode lugs, high contact resistances, and polarization because of the volume of slimes, were overcome, and several million pounds of anodes, as impure as the foregoing, of ordinary commercial size and shape, were successfully disposed of on a large scale at the plant of the Baltimore Copper Smelting & Rolling Co.

Unleached slimes, containing the bulk of impurities deleterious to a copper refinery, were sold to a plant equipped to recover the lead.

Costs, especially power costs, for refining such impure anodes, were considerably higher than for ordinary refining, but they were justified by the excellent metallurgical separations obtained.

#### ACKNOWLEDGMENT

The author acknowledges his indebtedness to the officials of the Baltimore Copper Smelting & Rolling Co., through whose courtesy permission was obtained to publish the above data, and especially to Mr. W. H. Peirce, president, and Mr. E. W. Rouse, general superintendent, under whose direction the work was carried on.

#### DISCUSSION

C. S. WITHERELL, New York, N. Y. (written discussion).—This paper is particularly valuable in that it gives the results of operations carried out under conditions differing from standard practice. In the electrolytic refining of copper, as in other kinds of metal refining, it is occasionally necessary to treat extraordinary foul or complex material, in which cases it is valuable to know what other metallurgists have accomplished under similar conditions.

As tapping the slimes-covered anodes brought the tank-voltage down to 0.45 to 0.50 volt, the counter electromotive force was probably not more than 0.1 or 0.2 volt; hence the so-called polarization was, mainly, caused by the accumulation on the anodes of a resistant covering of slimes and the built-up excess voltage was due to overcoming ohmic resistance.

This excessive ohmic resistance at the surface of the anodes may result from two causes: First, the slimes may be of colloidal nature and thereby constitute a nearly impervious film over the anode surface; second, the adhering slimes may act as a porous diaphragm and thereby imprison an anolyte film in contact with the anode surface, which

quickly builds up to the saturation point. After reaching saturation, naturally any sulfates formed by anodic corrosion must remain in the solid state and thus create a resistant coating. The latter phenomenon can be made much less effective by maintaining the electrolytic hot and dilute.

The author was cognizant of the benefit of a high electrolyte temperature, as shown by the paragraph at the bottom of p. 585. I am surprised that the  $C^2R$  effect did not heat the electrolyte above 135° F.

Electrolyte of a specific gravity of 1.255 to 1.285 is too concentrated for the conditions set forth in the paper. An electrolyte of a specific gravity of 1.20 to 1.22 and a temperature about 140° F. would greatly lessen the rate of voltage increase. This lower specific gravity would still permit of carrying sufficient copper and free acid (say 3 per cent. Cu and 11 per cent.  $H_2SO_4$ ) in the electrolyte and allow some leeway for accumulating nickel and other soluble ingredients, but the electrolyte would have to be replenished at about twice the rate.

C. P. LINVILLE, Elizabeth, N. J.—I conducted some experiments in a semicommercial way along the same line as the author mentions. Our first intention was to use high-nickel low-copper anodes for the purpose of taking nickel solutions, the idea being to increase the nickel at the same time that we reduced the copper in the solution. With the same class of material exactly, using a high-nickel liquor that we had, our voltage usually ran about 2, and we plated copper from the solution without dissolving from the anode anything to speak of. Maintaining a temperature of 150° with a dilute electrolyte, we were able to conduct this operation satisfactorily with about 0.2 volt. Our trouble was that after several days' operation the slime was built up so high as to make a high resistance.

M. H. MERRISS.—When the multiple-tank room was designed, no provision was made for running the temperature any higher than about 125° or 135°, so that I can furnish no data bearing on the temperature effect mentioned by Mr. Witherell.

With regard to the dilution of the electrolyte: The next step in the nickel recovery process was to decopperize the foul electrolyte from the multiple-tank room handling these anodes and then take it to the nickel plant for treatment. That decopperization was carried on at, say, 24 or 26 lb. per kilowatt-day, so the question of the relative economy of decopperizing more foul solution in order to keep the tank-room electrolyte low in specific gravity, versus handling it the way we did, is an economic problem that I cannot answer.

C. S. WITHERELL.—Did the temperature increase when the ohmic resistance increased?

M. H. MERRISS.—The temperature did not go over 135°. The temperature on the top of the tanks was much higher, as shown by the melting of the triangular bars, but not the temperature of the electrolyte. It is to be remembered that this was a comparatively small electrolytic tank room, with a great deal of solution coming into it every day and a great deal going out, which fact had a tendency to hold down the temperature. To only about 20,000 cu. ft. of electrolyte 1200 cu. ft. were being added each day, and 1200 cu. ft. withdrawn.

G. E. DALBEY, Middletown, Conn.—What method was used to remove the copper from this foul solution before taking the nickel solution away to recover the nickel therefrom?

M. H. MERRISS.—We electrolyzed it with insoluble (lead) anodes in the ordinary manner.

## Ammonia Leaching of Calumet and Hecla Tailings

C. H. BENEDICT AND H. C. KENNY, LAKE LINDEN, MICH.

(New York Meeting, February, 1924)

A 2000-ton ammonia leaching plant has been operated by the Calumet & Hecla Mining Co., at Lake Linden, Mich., continuously since February, 1917, except from April, 1921, to April, 1922, during the period of depression following the European war. A description of this plant has been published elsewhere.<sup>1</sup>

The present article describes the operation of the plant since 1917, together with the changes in the process that have been found to be advisable. In spite of the fact that this plant and that of the Kennecott Copper Co. are the only ones operating on a large scale, much experimental work is being done on ammonia leaching, as applied to oxidized ores, and it is to aid these and other investigators that this detailed account is given. For the benefit of those unfamiliar with the original article, the following short abstract is given, as an introduction to a more detailed account of the process and the reasons for present practice.

### RÉSUMÉ OF PREVIOUS ARTICLE

Leaching on a commercial scale began in July, 1916, and by February, 1917, the plant of 2000 tons capacity was in commission. The ore treated is a conglomerate containing native copper and no sulfides or oxidized copper minerals. Before leaching, the ore is crushed by steam stamps and Hardinge pebble mills to pass a 28-mesh screen. Free copper is removed, by gravity concentration, on Woodbury jigs and Wilfley tables, and colloidal slime for oil flotation is removed by quadruplex Dorr classifiers. The leaching sand remaining contains about 2 per cent. + 28-mesh material and 15 per cent. - 200-mesh and carries from 8 to 14 lb. of copper per ton, depending on the grade of ore worked. The solvent employed in leaching is a water solution of ammonium carbonate,

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<sup>1</sup> C. H. Benedict: Ammonia Leaching of Calumet Tailings. *Eng. & Min. Jnl.* (1917) 104, 43.



or rather a solution of copper ammonium carbonate; the chemistry of the leaching process is as follows:

Cupric ammonium carbonate + excess ammonium carbonate + native copper  $\rightarrow$  cuprous ammonium carbonate.

As native copper is the only valuable mineral present in the ore, advantage is taken of the two valences of copper in water solution to effect its oxidation to a soluble form; native copper is nearly insoluble in ammonium carbonate in the absence of an oxidizing agent. A portion of the cuprous solution is regenerated to the cupric condition for use as a new leaching solution by oxidizing it with air, viz.,

Cuprous ammonium carbonate + oxygen (air)  $\rightarrow$  cupric ammonium carbonate.

Copper recovery from the remainder of the cuprous solution is effected by distillation whereby the ammonium carbonate is volatilized and recovered and the copper precipitated as copper oxide, which is shipped to the smelter for refining. Theoretically, no reagents are lost and only the oxygen of the air is consumed in the process. Actually, slops, leaks, and inefficiencies account for a small amount of ammonium carbonate and, in the interests of capacity and economy, a certain amount is sacrificed in the sand tailing and waste solution from distillation.

The leaching is done in steel tanks 54 ft. in diameter and 12 ft. high, of which there were two rows of four each. A crane travels over each row of tanks for handling removable tank covers, sand distributers, and other appurtenances. The tanks are covered when containing ammonia solution, to prevent losses of ammonia by volatilization and also to keep down the objectionable odor. These are trussed covers of steel plate supported on the tank wall. A seal between cover and tank is made by a channel iron on the cover projecting into an annular launder on the tank filled with water; this prevents the escape of ammonia around the edges of the cover. The tanks are filled with sand by means of a portable distributor of the Butters & Mein type and are provided with side and bottom discharge doors. The sand in the tank is supported on a canvas filter stretched over cocoa matting resting on wooden grids. Downward percolation only is used in leaching.

Eighteen steel leaching-solution tanks, each 22 ft. in diameter by 11 ft. high, provided storage for all plant solutions; for storing concentrated ammonium-carbonate solutions, smaller steel tanks were used.

The leaching cycle, in 1917, was as follows: A tank was filled with sand from a launder to about 10 ft. 6 in. effective depth (1000 tons dry sand), the surface water was drained off, the surface leveled, and a layer of surface slime broken up. Cupric ammonium carbonate solution was flowed over the surface of the sand and allowed to drain down through it, displacing the contained water at as rapid a rate as possible. When ammonia solution appeared in the effluent, the waste valve was closed

and the percolation rate cut down to a predetermined figure. The effluent solution then was directed to the desired effluent main. When the correct volume of leaching solution had been allowed to flow on the sand, it was followed by a second solution lower in copper than the first, by ammonia wash, and then by water. The first effluent solution was low in copper and ammonia and, after oxidation, became a part of a new second leaching solution. Following this, the effluent solution was richer in copper and was sent to distillation, while from the remaining effluent, the leaching solutions and ammonia wash were built up.

In the distillation process, a special design of ammonia still, termed a roughing still, is employed. This consists of a cylindrical cast-iron vessel containing a series of horizontal shelves slightly concave, each shelf being provided with a scraping arm carried on a central shaft. Each shelf has an outlet and these outlets are staggered so that solution passing down through the still flows across each shelf in turn. Steam is admitted at the bottom of the still and flows counter-current to the solution through the same shelf openings. The heat of the steam raises the solution to the boiling point and the current of steam carries off through the outlet opening in the top of the still the ammonia and carbon dioxide volatilized by the boiling. The ammonia and carbon dioxide are then cooled and absorbed in water, to be used later in the leaching process. Copper oxide precipitates on the shelves of the roughing still and is scraped off by the revolving arms, passes down through the solution openings along with the solution, and is caught in a trap at the base of the still. These roughing stills are very efficient for removing copper oxide, but the waste solution from them is not barren and is run to a second unit, called a finishing still, which is an efficient ammonia still. Here the removal of copper, ammonia and carbon dioxide is complete.

In the original article, it was stated that the capacity of the plant was to be doubled; this extension was completed in the early part of 1918. The plant now contains sixteen 1000-ton sand leaching tanks in two rows of eight each and twenty-five solution storage tanks. The number of units in the distillation plant was increased from two to four. There is now ample capacity for handling all material of leaching grade produced by the stamp mills and reclamation plant. Whereas the capacity, according to the original cycle, was rated at 4000 tons daily, the changes have so reduced the leaching time that over 8000 tons daily has been treated and, if the feed were available, this capacity could be maintained.

#### LEACHING

The first difficulty encountered, after getting the plant into successful operation, was with the solvent power of the leach solution, on attempting to increase capacity. The sand tailing was not uniformly low in copper,

as was expected, and it was found that although the leaching solutions were of the proper concentration to do good work their action was not as rapid as it should have been and the copper concentration of the strongest effluent solution was lower than expected. This was correctly attributed to the lack of proper oxidation of the leaching solutions, a contingency that had been anticipated from the beginning of experimental work. After developing an analytical method to determine the ratio of cupric to cuprous copper in a solution, it was found that the cupric copper was surprisingly low; and as it is the cupric ammonium carbonate only that attacks native copper, efforts were made at once to oxidize the leaching solutions with air. After determining, by experiment, the proper size of equipment necessary, two steel towers were erected, each 8 ft. in diameter by about 35 ft. high, for oxidizing the copper; and a third, 6 ft. in diameter by 15 ft. high, for absorbing any ammonia carried away by the air passing through the oxidizing towers. These towers were filled with wooden grids so as to offer a large amount of film surface to the action of the air. The solution was sprayed on top of the grids, allowed to percolate through them, and drawn off at the bottom. Air was forced into the bottom, from a blower, and passed through the oxidizing towers in series and, finally, through the absorbing tower. One tower was provided for each leaching solution; and although, at present, only one leaching solution is used it is divided and flows in parallel through the two towers. Very little ammonia vapor is carried along by the air; but to recover this, a spray of water in the absorbing tower, amounting to 0.5 cu. m. per hr., is used. This, after absorption, becomes part of the ammonia wash. The losses of ammonia and carbon dioxide in the exhaust air are insignificant.

After installing the oxidizing equipment, the leaching power of the solutions increased markedly and, since that time, a practice has been made of keeping the cupric copper in the leach solution up to 90 per cent. of the total copper.

An excess of air is used, as may be judged from a recent experiment in which 100 cu. m. of solution carrying 34.5 gm. per liter copper, 61.9 per cent. of which was cupric, was oxidized and resulted in a solution containing 90.4 per cent. cupric copper. The air leaving the absorber contained 7.2 per cent. of oxygen, showing a removal of oxygen from the air of about 66 per cent. This excess of air is necessary to maintain a high cupric to cuprous ratio under varying conditions of volume and concentration.

No difficulties have been experienced with the apparatus and no corrosion is apparent. The absorbing water used contains considerable calcium chloride; and as the air carries carbon dioxide into the absorber, as well as ammonia, a precipitate of calcium carbonate forms on the grids, which must be removed occasionally when the back pressure on the apparatus becomes high.

With the oxidation of solutions accomplished, the plant was easily brought up to its rating of 4000 tons daily but the plants, preliminary to leaching, increased their efficiency and it became necessary to handle still larger tonnages. This meant a speeding up of the cycle, and the obvious way to do this was to increase the strength of the leaching solutions and to attempt to keep down the ammonia loss at the same time.

The leaching solution used, in most of the experimental work, contained about 12 gm. per liter ammonia ( $\text{NH}_3$ ), with carbon dioxide and copper in proportion. Soon after the start of commercial operation, it was realized that to obtain the proper extraction in the length of time allotted it would be necessary to increase the strength of the solution beyond that point so that a solution carrying 20 gm. per liter  $\text{NH}_3$  was adopted. This resulted in a loss of ammonia, in the sand tailing, of about 1 lb. per ton, as it was practically impossible to wash the tailing free. It was believed that the stronger the leaching solution the greater this loss would be, which proved to be the case. Demands on the plant for increased tonnage during the war years were met by increases in the strength of the leaching solution, so that the ammonia loss increased to about  $1\frac{1}{4}$  lb. per ton. With ammonia at 35 c. per lb. at that time, it became the greatest single cost and more than half of the total. A means of cutting down the loss without decrease in capacity was very much to be desired.

The use of steam for driving out ammonia from a residual product is a feature of early patents on leaching copper ores by ammonia, and the amount of ammonia remaining absorbed in the sand after washing was determined in the laboratory by this method. It was obvious that a successful application in the leaching tanks would result in marked economies of operation. The Kennecott Copper Co., operating an ammonia leaching plant in Alaska, had developed a very effective steam wash for its tailing. In this process, steam was admitted to a leaching tank above the body of sand and forced through the sand under pressure, volatilizing any ammonia contained therein, which was forced out through the bottom of the tank, condensed, and recovered. For this work not only were tight covers required but strongly reinforced covers.

During the early part of 1918, we made small-scale experiments with a view to using this process if it proved practicable. The objections at the start were obvious. The tank covers were not built to withstand pressure and no tight joint was provided; therefore, it would be necessary to design special covers, and to design a movable cover 54 ft. in diameter built to withstand 10 lb. steam pressure or a possible vacuum was an engineering problem in itself. Moreover, experiments showed that the pressure process was unsuited for the work. The sand is very fine and the sand bed, consequently, is not readily permeable. A fairly high pressure of steam was required to keep up the flow through the fine sand and the

time consumed in steaming was too great to make the process feasible. As the leaching tanks are not insulated to prevent heat radiation, a long steaming period would result in a high loss from this cause.

Before abandoning the attempt to recover the lost ammonia by steaming, a vacuum steaming process was tried, which proved successful. As put into practice, steam is admitted above the surface of the sand, in the leaching tank, at atmospheric pressure. A partial vacuum is maintained beneath the filter at the bottom of the tank and, because of the vacuum, steam is drawn into the sand bed. The cold sand condenses the steam, at first, and the vacuum is thereby increased, causing an augmented flow. As the mass becomes heated, the steam volatilizes the contained ammonia, which passes downwards with and is collected by the condensate. When the entire bed of sand has become heated, the suction is continued and steam is drawn through and condensed in a surface condenser. When the condensate becomes sufficiently low in ammonia, the flow of steam is stopped and water is allowed to flow over the sand surface. By the action of the vacuum pump, the water is drawn through the sand, becomes heated by it, and the first portion vaporized, so that an additional steaming effect is obtained in this manner. The vacuum treatment is prolonged until the effluent solution contains a low percentage of ammonia, usually 1 gm. per liter. Practically all of the adherent ammonia is removed from the sand in this manner. In Fig. 1 the effect of this steaming is shown graphically; there is an increased concentration of ammonia in the condensate and an equally rapid fall. The introduction of steaming did not, as anticipated, reduce the volume of solution distilled for copper recovery as the amount distilled had to be equivalent to the dilution, and this did not decrease to any great extent.

The following new apparatus was required: A steam main, four regular tank covers equipped with steam-inlet connections and automatic steam-control valves, expansion joints in the effluent wash line, a surface condenser with vacuum pump and condensate pump. The steam main has an outlet at each tank and the covers are moved from tank to tank as desired. The automatic control valve regulates the steam pressure over the sand to within 1 in. of water above or below atmospheric pressure, although the flow varies considerably and the only joint between tank and cover is the water seal used to prevent the escape of ammonia. The effluent wash line carries air, solution, and vapor to the condenser, the air being exhausted by the vacuum pump and used in the oxidizing towers while the solution and condensed vapor make up the bulk of the new ammonia wash.

Although the use of the steam wash did not result in a material saving in the amount of solution distilled, we were able to decrease this amount by a careful study of the factors controlling dilution. In leaching by

downward percolation, it is customary to use the piston method of displacement; that is, one solution in passing down through a charge forces another solution ahead of it and the first is displaced completely by the second. In the case in question, considerable dilution took place at the start where the water contained in the sand was displaced by the leaching solution. This dilution occurred through a mixing of the leach with the water, forming a solution too strong to waste. By draining the water originally contained in the sand just below the surface and by building up a head of leaching solution over the sand before percolation was allowed to proceed, the dilution could be kept down to a minimum. Leach solution used is displaced by wash and wash by water in a similar manner. Later, it was found that tanks that filled unevenly gave more dilution trouble than others and also higher tailings; all tanks are now carefully leveled before leaching by means of a rotating water-jet apparatus. In running solution on to a tank, care must be taken that it does not form holes in the sand or uneven percolation will result.

The leaching cycle used in 1917 provided for two leaching solutions, called the first and second leach. The idea was to have a solution of weaker solvent power act on fresh sand and to become saturated with copper; this to be followed by a more active solution that would dissolve the last traces of copper. A better understanding of the chemistry of the process showed that there was little, if any, difference in the activity of the two solutions, so to simplify the operation the two leaches were gradually brought to nearly the same strength. About the time that steaming was introduced, the two solutions were thrown into one and only one leaching solution is now used. This is the proper procedure, as it is the cupric copper that does the leaching and an excess of ammonia over the proper ratio is of no advantage. A solution of the proper strength will become practically saturated in passing through fresh sand, so that nothing is gained by the two passes. The ammonia wash is still used but is obtained in a different manner; namely, as the solution drawn from the condenser during the steaming operation. This wash is relatively high in ammonia and low in copper, the usual ratio being 3:1 by weight. The steam wash is preceded and followed by a water wash. Enough wash must be used to remove all dissolved copper before the sand becomes heated by the steam or copper will be precipitated in the sand. The wash must be reasonably high in ammonia and low in copper, or the copper in the leaching solution will hydrolyze on dilution and basic copper carbonate will be precipitated. Originally, the rich, or pregnant, solution for copper recovery was drawn from that portion of the effluent solution that was richest in copper; and to this was added enough of a weak solution to make the total equal to water introduced into the cycle and to keep the volume of the solutions constant. By this method, considerable solution containing cupric copper was sent to the

stills and it was difficult to prevent the formation of basic copper carbonate during the distillation. This depleted the solution of carbon dioxide, lowered the grade of the concentrate, and formed in the stills a hard scale that was difficult to remove. According to present practice, the first portion of the effluent solution is used for distillation. This solution, having acted on fresh copper-bearing sand, is practically all in the cuprous state; the volume distilled is such that the proper amount of copper is removed and at the same time the volume of leaching solution is kept practically constant. The precipitated oxide is largely cuprous and

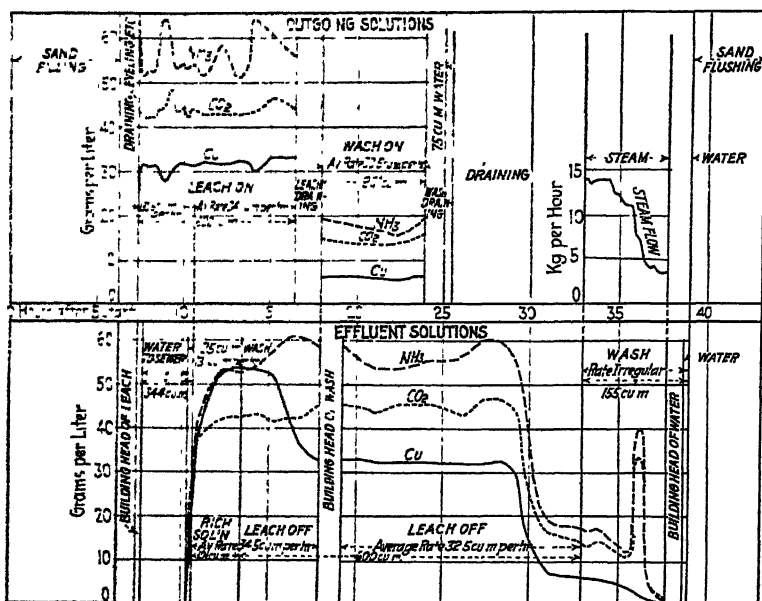


FIG. 1.—TYPICAL LEACHING CYCLE.

causes much less caking. Usually, a few cubic meters of the first effluent solution is sent to the ammonia wash, but this is done merely as a convenience to keep calcium carbonate from forming in the long rich solution lines; the wash lines are shorter and usually hot, so that the tendency there is for the calcium carbonate to remain in solution. Trouble from calcium-carbonate scale is discussed later.

After the requisite amount of rich solution for distillation is drawn off, the remainder of the effluent solution, before steaming, goes to make up the new leaching solution. It passes through the oxidizers on its way to the storage tanks and is brought up to strength before going on to the sand by mixing with strong ammonium-carbonate liquor, obtained either from distillation or as new liquor from tank cars. A sand tank is drained

thoroughly before steaming and effluent solutions following this make up the new ammonia wash.

To indicate the cycle used at present, an individual tank has been followed through, as shown in Fig. 1. Strengths of solution are shown, also the principal events in the cycle as they occur. This tank, taken at random, is typical but no two tanks are exactly alike. The filling time, as shown, is 6 hr., which is much longer than the average. A solution flow sheet, Fig. 2, shows the course taken by the various solutions concerned.

The difficulty in keeping the solutions at the point of maximum efficiency may be realized from a consideration of the following factors which must be controlled.

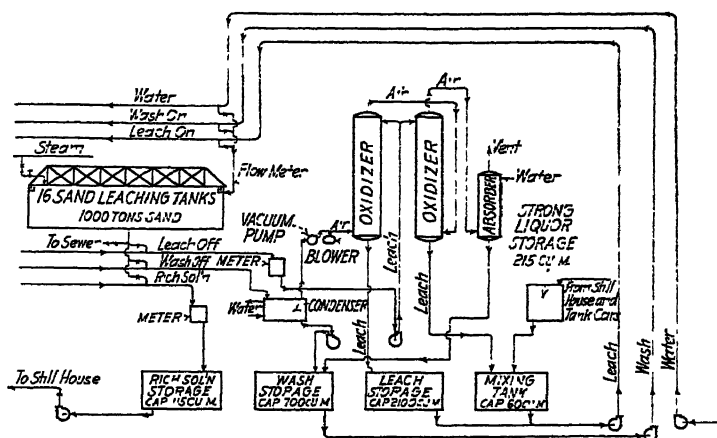


FIG. 2.—LEACHING SOLUTION FLOW SHEET.

**Concentrations.**—Copper in leach (30 gm. per liter); regulated by removing for distillation an amount of copper equivalent to that dissolved from the sand by the leaching solution.

Ammonia in leach (60 gm. per liter); strong liquor added to leach in required amount.

Carbon dioxide in leach (40 gm. per liter); tank-car shipments must be carbonated as required; slow adjustments only are possible.

Ammonia to copper ratio of wash (3  $\text{NH}_3$ :1 Cu); regulated by amount of first water wash used before steaming.

**Volumes.**—Volume of leach must be kept within limits of storage tanks and sufficient for unusual demand; excess volume, if any, distilled, deficiencies made up from rich solution and wash.

Volume of wash is regulated by amount of water before steaming, also by amount drawn off at end of cycle.

Volume of strong liquor is regulated by tank-car shipments.



*Oxidation of Leaching Solution.*

Kept to 90 per cent.

Assay of feed and tailings for the tank shown in Fig. 1 are as follows; they are typical of practice on richer sands:

	PER CENT. SAND	PER CENT. COPPER IN FEED	PER CENT. COPPER IN TAILING	PER CENT. EXTRACTION
+ 28 mesh.....	2.1	0.731	0.354	51.6
+ 48 mesh.....	17.7	0.547	0.180	67.1
+ 100 mesh.....	50.5	0.550	0.111	79.8
+ 200 mesh.....	15.5	0.579	0.092	84.1
- 200 mesh.....	13.9	1.171	0.107	90.9
Average.....		0.648	0.123	81.0

**DISTILLATION**

The distillation process, in its simplest terms, consists in driving off the ammonia and carbon dioxide by means of live steam, as gases, condensing them after a partial concentration, and collecting the precipitated cuprous and cupric compound, chiefly oxide. If copper oxide were produced in one step from the solution, the operation would probably be very simple; but both copper hydrate and carbonate are intermediate products and, when precipitated, are inclined to produce a hard scale. Early in the work, it was realized that cupric-copper solution produced more carbonate than cuprous solutions and gave more scale trouble, but it was not until recently that it was found that a hydrate scale could be as troublesome as the carbonate and the dehydration of the copper hydroxide is not as simple as it would appear. On long-continued boiling, the dehydration proceeds to a point where little scale results, for which reason, in a single-effect still, the oxide is usually soft if boiling is long continued. In a continuous still, however, there is always some point where hydrate is precipitating and here scale forms. On the other hand, a continuous still has much to recommend it as far as capacity and economy are concerned. The ordinary type of continuous ammonia still becomes choked with a hard scale and is difficult to clean, so the roughing-finishing still combination was developed.

The roughing still takes care of the solution while copper hydrate forms, and the finishing still, an efficient ammonia still, receives from the roughing still lean solution and some dehydrated oxide, which causes little scale trouble. The roughing stills are provided with clean-out doors and are split vertically. Once a week, the doors are opened and scale removed as far as possible; and once in six weeks, the vertical joint is broken, one-half of the still removed, and the whole given a thorough cleaning. The scraping arms, driving mechanism, piping, etc. are attached to the fixed half of the still and are not disturbed. Considerable foaming takes place during operation and all pipe lines carrying solution or vapor become filled with scale and require frequent cleaning.

There are four units, each unit consisting of one finishing still, two roughing stills, one reflux condenser, one ammonia condenser, and the necessary accessories. The feed liquor, rich solution from the leaching plant, enters at the top of the roughing stills and flows through them to the finishing still. The major portion of the precipitated oxide is removed by a trap, which is discharged intermittently and is located at the base of the roughing still. The waste liquor from the finishing still is pumped to Sweetland filters, where suspended oxide is removed and the barren liquor rejected. Steam enters at the base of the finishing still; from the top of the roughing still, the vapor carrying ammonia and

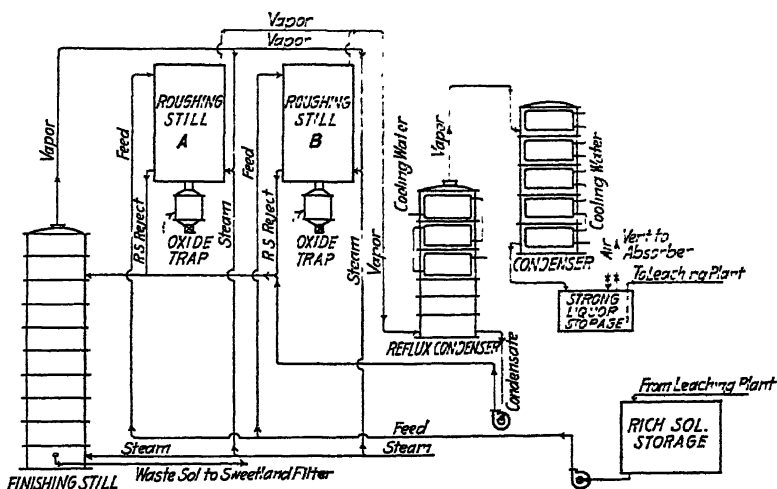


FIG. 3.—FLOW SHEET OF STILL UNIT.

carbon dioxide gas passes on to the reflux condenser where it is partly cooled. By the cooling, some condensation takes place; and as the condensate is low in ammonia, the resulting vapor is enriched. The condensate from the reflux is returned to the finishing still and the vapor is further cooled and condensed in the ammonia condenser and flows to strong-liquor storage tanks. The temperature of the vapor leaving the reflux column controls its grade in ammonia and is kept constant. A diagrammatic flow sheet is shown in Fig. 3.

The solution distilled at present averages about 35 gm. per liter copper, 35 gm. per liter ammonia, and 30 gm. per liter carbon dioxide. The strong liquor carries no copper, about 150 gm. per liter ammonia, and 130 gm. per liter carbon dioxide. The effluent solution from the roughing stills carries 2 or 3 gm. per liter ammonia and the finishing still waste about 0.05 gm. per liter. Steam consumed including all losses is approxi-

mately 500 kg. for each cubic meter of solution boiled out. The ammonia is practically all recovered in this operation, the loss in the waste being slight and incidental leaks easily detected.

Although the usual type of column still is apparently unsuited for boiling out the liquor, the fact that it is much more efficient than the roughing stills led to making some experiments with a modified type. This is practically an ordinary continuous ammonia still except that the openings and clearances are larger. By a careful control of concentrations, the formation of copper carbonate is prevented; and by controlling temperatures and pressures, the dehydration of the copper hydroxide is facilitated. Many other unusual factors entered and had to be cared for. One unit consisting of a column still, a reflux column, and a condenser is now operating very satisfactorily. Careful regulation is necessary but the capacity is higher than that of the old type of unit and the steam economy is much improved. In this still, the copper oxide is kept in suspension by the internal agitation and passes out through the still with the waste liquor to a Sweetland filter. More frequent cleaning is necessary than with the old type of unit, but this operation is concentrated in one piece of apparatus and is more easily accomplished than before. Experiments are being continued, and with a better understanding of the conditions under which the scale forms it may be possible to prevent the formation of any great amount. This type of unit will probably replace the older form.

In a process of this description, there are many incidental factors that are worthy of note but that do not bear directly on the operation as carried out. The two great difficulties with most leaching operations are corrosion and fouling, and while ammonia leaching is not handicapped in this direction to the extent that an acid leaching process would be, care is necessary in the choice of materials of construction and in the details of manipulation.

Because of corrosion, zinc, brass, and copper cannot be used in any parts coming in contact with the ammonia. The solution used for leaching has very little, if any, corrosive effect on iron although iron rust seems to be softened by it. Leaching tanks and solution-storage tanks of steel show no bad effects, provided that care was taken to have good rivets and joints when the tank was built; rust joints are not permissible. Cast-iron pipe lines with flange joints have been chiefly used and have the advantage that there are no threaded joints to leak.

Strong ammonium-carbonate liquor is quite corrosive, especially when hot or when carrying a small amount of copper in solution. Steel tanks and pipe lines are not permissible for strong liquor; for storing and conveying this liquor, cast iron is used as this seems to be more resistant than steel and is considerably heavier. Where thin pipes are required, as in condensers, aluminum is used as it resists the action of the solution

very well. Pumps cannot be used to good advantage on strong liquor, so that storage tanks are made heavy enough to withstand air pressure and the solution is removed by this means.

Although copper-ammonia solutions are supposed to have a dissolving action on cellulose, filter cloths and cocoa mattings show no bad results from this cause. Copper-ammonia carbonate seems to have no action of this kind and the concentration of the solution is such that no copper-ammonia hydrate is present. Copper-ammonia hydrate would doubtless dissolve this material.

Freedom of fouling, from the building up of dissolved minerals from the ore, was not to be feared because the solvent is regenerated by distillation. In fact, no fouling of any description was expected; but during the winter of 1917-18 the efficiency of the plant began to fall off for no apparent reason. The copper content of the tailings increased from 0.100 per cent. in August, 1917, to 0.164 per cent. in December, and this was accompanied by an irregularity in the percolation rate indicating that all parts of a charge were not leached uniformly. Standard practice had been not to flush out the leached sand tailing completely from the tank but to leave a few inches in the bottom as a protection for the filter cloth beneath it. The disadvantage of doing this was not apparent at the time, but since it was never removed the condition of the filter cloth could not be ascertained. When it was realized that something was interfering with good work, the sand layer was removed from the bottom of a tank and it was found that the filter cloth was impregnated with a nearly impervious layer of calcium carbonate. Although calcium-carbonate scale had formed occasionally in pipe lines, it had never caused any serious trouble. Treatment with dilute hydrochloric acid removed the scale from the filter and, after going over all the leaching tanks in this manner, the plant operation became normal again, although the treatment had to be repeated in about three months. Later when the leaching cycle was changed, for other reasons, it was found that the pipe lines carrying the first portion of the effluent solution from a leaching tank became coated and finally choked with the same kind of scale, and that trouble from this source was much more serious in winter than in summer. It was found that calcium salts were introduced into the solution by way of the water supply, which contained considerable calcium chloride and sulfate. In displacing the water originally present in a sand charge with ammonium-carbonate solution, a certain amount of mixing took place and calcium carbonate formed, being the most insoluble calcium salt. The solubility of calcium carbonate in water is given in handbooks as 0.0018 per cent. at 15° C., whereas at 100° C. it is 0.088 per cent. soluble, which explains the winter trouble.

Several methods of attacking the scale formation were developed. For removing scale from filter cloths, hydrochloric acid is still used.

	1920		1921	1922	1923	
	1ST HALF	2D HALF	1ST QUARTER	LAST 3 QUARTERS	1ST HALF	2D HALF
Tons treated.....	612,010	721,770	349,070	1,353,654	741,000	923,130
Pounds copper produced.....	5,776,368	5,104,372	3,695,136	10,455,000	6,171,000	7,454,000
Cost per ton sand.....	41.76	43.59	50.16	29.53	36.73	32.25
Cost per pound copper.....	4.42	6.21	4.74	3.86	4.41	3.99
Recovery pounds per ton.....	9.41	7.07	10.59	7.72	8.33	8.07
Assay of oxide.....	52.50	51.45	51.73	52.33	52.05	52.55
Assay feed.....	0.592	0.453	0.624	0.488	0.521	0.507
Assay tailing.....	0.124	0.106	0.125	0.108	0.108	0.103
Per cent. extraction.....	79.1	76.6	80.0	77.9	79.3	79.7

## DISCUSSION

G. E. DALBEY, Middletown, Conn.—Some time ago, I was interested in recovering copper from tailings from a concentrating plant that was using brass-foundry ashes, and similar refuse. Some of the tailings went about 2 per cent. of copper, some of it was combined as a brass, very fine, and some of it was oxide copper. We constructed a plant and pumped the ammonia liquor round and round, but the ammonia loss was so high that we discontinued the work. What type of oxidizers were used in this plant and how were the oxidizing gases washed? That was our principal trouble, recovering the ammonia.

C. H. BENEDICT.—Some details are given in the paper as to that. By using a moderate amount of air and running the liquor to be oxidized over grids, in other words, breaking it up into a fine stream and then running the air from the oxidizers through one absorber, you should get along without any great ammonia loss. That has been our experience. There must have been something wrong in the way your plant was connected up.

## Calculating the Zinc for Desilverizing Lead Bullion by the Parkes Process

BY GEORGE G. GRISWOLD, NEW YORK, N. Y.

(New York Meeting, February, 1924)

THE Parkes process of lead refining is based on the fact that when zinc is mixed with molten lead bullion, it forms an alloy with the silver and gold. This alloy freezes at a higher temperature and is of a lower specific gravity than the lead. With proper regulation of the temperature, the alloy solidifies and floats on top of the lead bath, from which it is removed and the silver, gold, and zinc recovered. The alloy should contain the maximum amount of silver ( $\text{Ag}_2\text{Zn}_3$ ).

The usual practice is to make two additions of the zinc. The first addition gives an alloy, or zinc crust, the zinc of which is saturated and is treated for the recovery of its zinc and silver; the crust from the second addition contains an excess of zinc and is used for the first addition on the following kettle. The crust produced depends on a number of items: purity of bullion, temperature, care with which kettle work is performed, addition of zinc, pressure used in expelling lead from crust, etc.

It is desirable to make the concentration of silver in the zinc crust as high as possible; otherwise an undue amount of byproducts is produced, which greatly increases the cost of refining. It was formerly considered good practice to make a concentration of 20:1. That is to say, if the lead bullion assayed 150 oz. doré per ton, the assay of the retort bullion recovered from the zinc crust should be 3000 oz. per ton. As a matter of fact, the concentration should never, except on bullion assaying over 300 oz., be so low, and with low-grade bullion it should be 50:1.

In one lead refinery where, ordinarily, the work was good, on a bullion averaging about 200 oz. per ton, a concentration of 24:1 was common; but how it was obtained was known only to the foremen. Changes occurred, and under new foremen the kettle work fell off badly; the problem then was to bring about this greater concentration. As is customary, the refinery had a "schedule" for its 60-ton kettles, which gave the number of pounds of zinc required for all possible assays, on both the first and the second zining. Using this schedule, high temperatures

were tried both in adding the zinc and in pressing the zinc crusts, but no appreciable increase in the grade of the retort bullion resulted. Decreasing the amount of zinc added resulted in silver losses. Finally, it was found that by cutting off a liberal poundage of zinc from the scheduled amount for the first zincing, the grade of the retort bullion could be controlled. Frequently, after pressing off the zinc crust, the assay of the kettle was found too high and an extra zincing was required. As the kettle work was a contract job and was supposed to be cleaned up in not less than 10 hr., the refinery was beset with labor troubles, and that at a time when labor was scarce.

It occurred to the author that it might be possible to work out a method for figuring the weight of zinc to be added for the first zincing on the basis of the total silver in the kettle. This would be, of course, the amount in the charge tapped from the softener, plus that added in the form of crusts, or stubs, derived from the second zincing of the previous charge. A start was made by assaying, for zinc and silver, a series of kettle samples after pressing off the crust from the first zincing. The zinc content of the kettle after skimming was found to vary with the silver content, and from the data thus obtained it was possible to calculate, with sufficient accuracy, the zinc content of the kettle, from the silver assay of the hot sample.<sup>1</sup>

Previous experiments on the zincy lead going to the refiner after complete desilverization gave an average of 50 tons per kettle and an average zinc content of 0.52 per cent.; therefore, 520 lb. of zinc per kettle went to the refiner. From these data the pounds of zinc available in the stubs could be calculated; thus:

$$\begin{aligned} \text{Let } x &= \text{tons material in kettles after pressing off first crust} \\ y &= \text{per cent. zinc in kettles after pressing off first crust} \\ z &= \text{pounds zinc added to remove all remaining silver} \\ xy + z - 520 &= \text{pounds of zinc in stubs} \end{aligned}$$

This formula was replaced after a few months by the empirical formula:

$$\frac{\text{assay of hot sample} + \text{assay of cold sample}}{2} \times \frac{x}{5} + z$$

The formula was suggested by Guy Cheney, who noticed that the ratio of the average silver assay to available zinc remaining after first zincing was a constant. As it gave identical results and was simpler, it was adopted. The formula is general and applies to any kettle, regardless of capacity.

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<sup>1</sup> The *hot sample* represents the total contents of the kettle; the *cold sample* represents the contents of the kettle after the zinc crust is removed.

To calculate the zinc required for the first zincing, one must first determine the total silver in the kettle. Let us assume that it is required to figure the zinc on a new charge; that the assay of the 60 tons of bullion tapped from the softener is 200 oz. per ton, the hot assay of the kettle from the previous charge is 100 oz. per ton, the cold assay 20 oz. per ton, that 2000 lb. of zinc has been added, and that  $x = 65$ .

$60 \times 200 + 100 x = \text{total to be zined} = 18,500 \text{ oz.}$

$18,500 \div 6.5 = \text{pounds zinc required for first zincing} = 2850 \text{ lb.}$

$12 \times 65 + 2000 = \text{pounds zinc available in stubs} = 2789 \text{ lb.}$

New zinc to be added 70 lb.

If the softened bullion assayed 100 oz. per ton, the total silver to be zined would be 12,500 oz., and the zinc required for first zincing would be  $12,500 \div 5.2 = 2404 \text{ lb.}$

As there is available in the stubs 2780 lb. of zinc, all the stubs will not be needed. An inspection of the number and size of the stubs should give a basis for a sufficiently close estimation of the zinc content of the fifth stub, assuming that there were five. If we assume the estimated content at 400 lb., there is required the first four stubs and 24 lb. new zinc for the first zincing. If the second zincing calls for 2000 lb. of zinc, there is added the fifth stub and 1600 lb. new zinc. This does not affect the assay as practically all the silver is in the first three stubs removed.

To apply this method successfully it is necessary: (1) That the bullion be thoroughly softened. (2) That the softened bullion tapped to the kettle be cooled down and liquated to remove copper. (3) That the capacity of the kettle at various levels be known. (4) That stubs be returned to their proper kettle.

The factors used above (6.5 and 5.20), were developed by experience, and ran from 5 to 8 according to grade of bullion. That they vary is probably due to the fact that at the pressing temperature, 780° F., the amount of zinc in solution is the same in all cases. Were this accurately determined and allowed for, the factor for silver would doubtless be the same for all grades of bullion.

The tonnage of the material in kettles was figured as for lead, and while the tonnage was probably wrong, the error was a constant. It would be desirable to know the specific gravity of the alloy at the temperature used. For the second zincing one may use a schedule or calculate.

Our knowledge of the rate of decrease in zinc and silver of the kettle content while working it down is meager. The author had intended to carry out a series of experiments to get this desired information, but labor and other conditions prevented. Exact information along these lines would be valuable. To obtain it is a work that might well be undertaken by metallurgical students where apparatus is available.



The following method of procedure is suggested: Remove the crust which forms immediately after the second addition of zinc; heat the kettle to insure complete solution of the zinc; stir and, when thoroughly mixed, take a series of gumdrop samples out of the stream flowing from stirrer; cool down and remove the second stub; again raise the temperature, stir, sample, etc., as before; follow this procedure until the desilverization is completed. Because of the pronounced tendency of this alloy to segregate, only in this way can concordant results be obtained. For the same reason, each gumdrop should be rolled and the whole dissolved, aliquot portions being taken for silver and zinc assays.

## DISCUSSION

C. S. WITHERELL, New York, N. Y. (written discussion).—The Parkes process is by far the process most generally used for desilverizing lead bullion, yet the main feature (*i. e.*, the application of zinc to the softened bullion for desilverizing) has always been done in the most unscientific and irrational method possible. Each lead-refinery operator has a pet "schedule" that is supposed to guide him as to the amount of zinc to use for each successive skimming from kettle, based on assays and kettle capacity. The formulas used for compiling most of these schedules seem to have absolutely no relationship to the chemical, physical, or metallographic properties of the metals and alloys involved.

Time is therefore over ripe for some one to put this matter on a rational basis and explain the fundamental properties that affect the consumption of zinc and the composition of the successive skims.

The author has had many years of experience with the Parkes process and, from my long acquaintance with him, I am certain that he is competent to undertake such a task; but, after reading his paper, I am led to the conclusion that he has written but little that clarifies the subject, in fact he has substituted one rule-of-thumb method for another.

The author should state that the insolubility of the Ag-Zn alloy in molten lead saturated with zinc is also a cause of separation. If one is not convinced of the importance of this property let him add some silver-zinc crust to a kettle of zinc-free refined lead; he will find that the molten lead at any temperature will promptly dissolve a considerable amount of both silver and zinc.

The author states that "the alloy should contain the maximum amount of silver ( $\text{Ag}_2\text{Zn}_3$ )."

 By this, I suppose, he means that the crust (first skimming) which is passed on to the next step in the process (retorting) should assay as high as possible in silver. The crust is not a single alloy but a heterogeneous mixture of silver-zinc alloy, zinc, probably some ternary combinations, and entrained liquidus from the kettle charge that pressing was unable to remove. Naturally if this crust is taken off

relatively hot and the zinc to produce it is limited, the Ag-Zn constituent will predominate.

The chemical formula  $\text{Ag}_2\text{Zn}_3$  that the author gives without qualification as the composition of the Ag-Zn alloy is open to question. H. O. Hofman quotes two alloys; first, an unstable alloy  $\text{AgZn}_5$ , second, a stable alloy  $\text{Ag}_4\text{Zn}_5$ . Referring to recently published equilibrium diagrams<sup>2</sup> it will be noted that although  $\text{Ag}_2\text{Zn}_3$  is shown as a stable single constituent with the melting point  $665^\circ\text{C}$ ., there exists also a stable constituent of a composition 29 atom per cent. (40.3 wt. per cent.) Ag melting point  $636^\circ\text{C}$ ., which is approximately  $\text{Ag}_3\text{Zn}_5$  and that this constituent is produced or forms part of a solid solution upon freezing any molten mixture of Ag and Zn from 37 atom per cent. Ag down to 1 atom per cent. Ag. It therefore would appear that the compound  $\text{Ag}_2\text{Zn}_3$  is the most likely to be formed when zincing at temperatures not extremely far above  $420^\circ\text{C}$ ., and would be the first constituent to separate upon cooling.

Referring to the third paragraph on first page, an additional and probably more important reason for maintaining high concentration of silver in the first zinc crust is the fact that the smaller the amount of zinc sent to retorts the smaller will be the amount of retorting and the smaller the zinc loss per ounce of silver produced.

The concentration-ratio on the first page is of little value unless taken in conjunction with the grade of bullion treated. A table of assays of retort-bullion or concentration-ratios corresponding to varying grade of lead-bullion treated according to good up-to-date practice, say for grades 25, 50, 100, 150, 200, 300, 400 oz. doré per ton, would be most valuable, especially if in the same table the corresponding zinc-to-silver ratios in crusts sent to retort were given.

The empirical formula, on the second page,

$$\frac{\text{Assay of hot sample} + \text{assay of cold sample}}{2} \times \frac{x}{5} + z$$

equals pounds of zinc in stubs, appears illogical, because the only reason one can obtain an assay of a cold sample less than the assay of the hot sample is due to the available extra zinc dissolved by the molten kettle charge at the higher temperature, which zinc when given up during cooling takes silver with it. Hence, the greater the amount of extra zinc dissolved, the greater will be the amount of silver extracted due to cooling; conversely, the greater the amount of silver extracted during cooling, the greater must have been the amount of extra zinc dissolved when hot. A more logical formula would be one based on the difference of assays hot and cold.

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<sup>2</sup> Dr. W. Guertler: *Metallographie*, 1, I, 474; H. C. H. Carpenter and W. Whitely: *Jnl. of Metallography*, 3, 145.

The author does not explain how he obtains the value  $z$ . I suppose this is in some way related to the assay of cold sample, as it represents the quantity of zinc added to insure practically complete removal of the remaining silver.

To determine the amount of zinc required for the first zincing, the author divides the total silver contents of the kettle after adding stubs by a divisor that is variable and dependent on grade of bullion, but determined by experience. This appears to be getting back to the rule of thumb; furthermore he does not give any means of determining the factor for any other grade of bullion or silver contents of kettle than the two cases cited.

I believe that, by a closer consideration of what takes place during the first zincing, a simple rational formula can be evolved as follows: The total zinc added for the first skim is disposed of in two ways: a part goes to saturate a hot molten charge still containing a part of the silver, the remainder forms the crust. The formula then would have the form  $z = \frac{A}{c} + b$ , wherein  $z$  is the amount of zinc,  $A$  is the total silver contents of kettle,  $c$  is a constant, and  $b$  is the amount of zinc necessary to saturate hot kettle charge at a given assay and temperature. Assuming that the values, given in the paper, of 2850 lb. zinc for 18,500 oz. silver and 2404 lb. zinc for 12,500 oz. silver are correct, the formula just given becomes for that case:

$$z = \frac{A}{13.43} + 1473, \text{ for 65 tons kettle charge, or}$$

$$z = \frac{A}{13.43} + 22.66K, \text{ for } K \text{ tons kettle charge, or say}$$

$$z = 0.074A + 23K \text{ for } K \text{ tons kettle charge at } 420^\circ \text{ C.}$$

Well-pressed skims that are sent to the retort, produced from 100 oz. to 300 oz. lead bullion, contain from 0.18 to 0.12 lb. Zn per ounce doré, hence the factor 0.074 would indicate that from 40 to 60 per cent. of the doré contents of the kettle would be removed in the first or hot skimming. At  $420^\circ \text{ C.}$ , the molten kettle charge will hold about 23 lb. of zinc per ton when in equilibrium with silver (about 100 oz. per ton). At the eutectic temperature of the lead-zinc system,  $318^\circ \text{ C.}$ , molten lead holds about 12 lb. of zinc per ton (authorities are not in accord) and practically no silver.

It is to be noted from the foregoing that the increase of 11 lb. (23 over 12) of zinc and 100 oz. silver is approximately equivalent to dissolving the compound  $\text{Ag}_2\text{Zn}_3$ . Unfortunately, on cooling more zinc leaves the molten charge than that which corresponds to  $\text{Ag}_2\text{Zn}_3$ ; hence when the eutectic temperature is approached, a considerable quantity of silver remains in the charge without sufficient excess or available zinc to form a crust. For this reason, it is necessary at this stage to add a reasonable

amount of zinc to insure complete desilverization. It is found that 0.3 to 0.6 lb. of zinc is required per ounce of silver contained in the skims produced by the second or cold skimming.

The work that the author recommends would be very interesting and valuable for the students, but I doubt if the data obtained from one grade of bullion would be of much help to an operating metallurgist in charge of a plant treating a different grade of bullion. It would be of far more value, and give something of greatest need, if some expert metallographist (somewhat more than a student) would accurately determine the equilibrium diagram of the ternary alloy Pb-Zn-Ag at the high Pb corner covering the ranges Zn, 0 to 3 wt. per cent., by steps of 0.1 per cent., and Ag, 0 to 3 wt. per cent. (0 to 900 oz. per ton), and put the information into such form that it can be easily understood and used by a lead-refinery operator.

Some metallographic work has been done by R. Kremann and F. Hofmeier.<sup>3</sup> The work is far from complete, no attempt is made to construct a working equilibrium diagram with isotherms. About the only thing the authors accomplished was to establish roughly the ternary eutectic curve at the Pb corner. They, however, give an interesting metallographic theory of the Parkes process zincing with which I do not entirely agree.

From information given in this article and from other sources I constructed the diagram shown in Fig. 1. The isotherms are plotted from very meager data, but, although the whole ternary diagram may be far from accurate it illustrates the essential features. The Kremann and Hofmeier theory is based on the assumption that when a molten ternary alloy Pb-Ag-Zn high in Pb is cooled, Ag-Zn separates constantly in the same ratio as existed in the original alloy. Therefore the point that represents the composition of liquidus moves along a radian, drawn through the point Pb, toward Pb until the eutectic curve is reached, from then on the particular ternary eutectic that the point reached continues to freeze without change of composition.

Assume a lead bullion containing Ag represented by point  $a$ , Fig. 2, and, for simplicity, assume that stock zinc is added; then the composition will change according to the line  $aa_1$  almost parallel to the Pb-Zn line. The point  $a_1$  represents the composition at the completion of the first zinc addition and the temperature will have to be raised to hold all in molten solution. On cooling, Ag-Zn will separate along the line  $a_1e_1$ . When  $e_1$  is reached, add zinc and heat; the composition will then change along line  $e_1a_2$ . Again cool and Ag-Zn poorer in Ag will separate

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<sup>3</sup> "Das ternäre System Silber-Zink-Blei, Ein Beitrag Zur Theorie des Parkesierens," *Monatshefte für Chemie* (1911) **32**, 563; Vienna. Kaiserlichen Akademie der Wissenschaften.

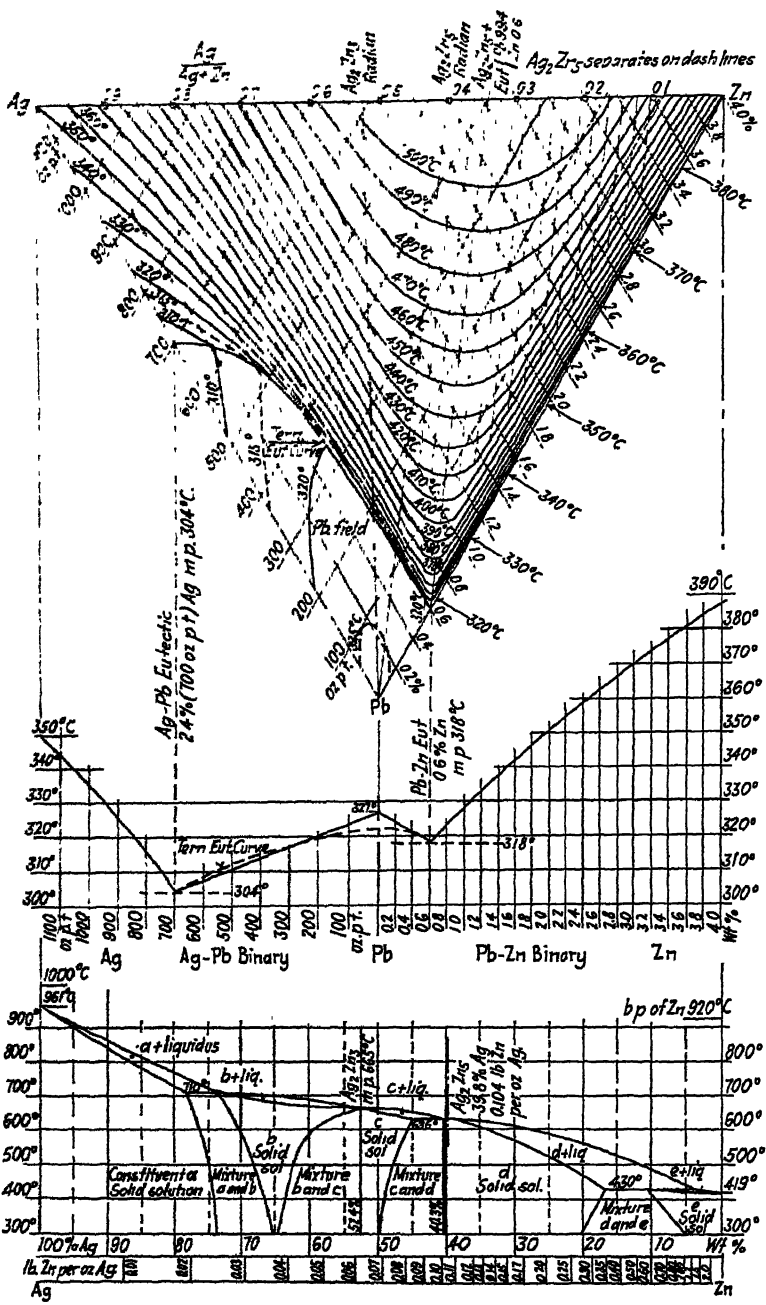
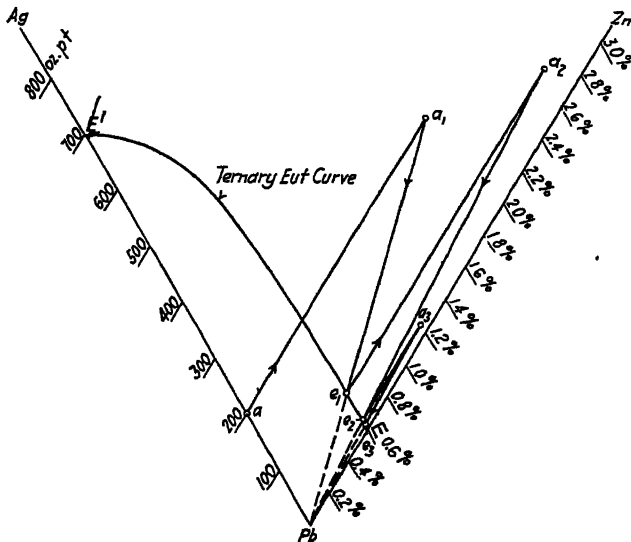


FIG. 1.—EQUILIBRIUM DIAGRAM NEAR Pb CORNER, Pb-Ag-Zn TERNARY, FOR APPLICATION TO PARKES PROCESS ZINCING. PLOTTED BY C. S. WITHERELL FROM DATA OBTAINED FROM VARIOUS SOURCES. Ag-Zn BINARY DERIVED FROM DIAGRAM BY CARPENTER AND WHITELEY.

along line  $a_2e_2$ . By repeatedly going out on a parallel and returning to the eutectic curve on a radian, the Pb-Zn line is approached; that is the Ag is removed as a Ag-Zn alloy successively poorer in Ag, but unchanged during any one cooling.

My objections to the theory are as follows: Practice proves that the alloy (or mixture) that separates first when the charge is hot is richer in



Assumed conditions and calculated data:-

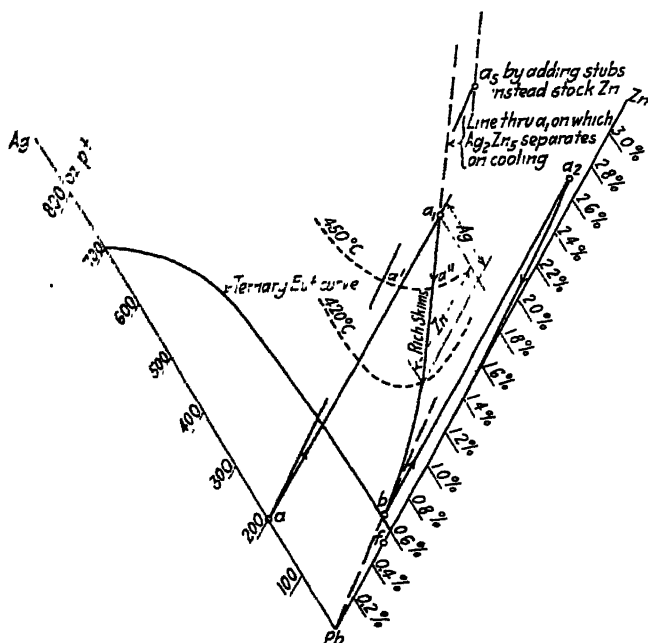
Point	Oz. p.t. Ag	% Zn	m.p. °C	Zn added lb p.t.	Radiance	
					Ag Ag+Zn	lb Zn/lb Ag
a	2000	0.000	320	—	—	—
a <sub>1</sub>	196.3	1.855	468	37.8	0.266	0.189
a <sub>2</sub>	63.3	0.587	321	—	—	—
a <sub>2</sub>	62.1	2.672	457	41.6	0.075	0.844
e <sub>2</sub>	14.2	0.600	319	—	—	—
a <sub>3</sub>	14.1	1.193	364	12.0	0.039	1.686
e <sub>3</sub>	7.1	0.600	319	—	—	—

Each successive treatment with 1/2 lb Zn p.t. halves the Ag.

FIG. 2.—GRAPH OF PROCEDURE OF PARKES PROCESS ZINCING, ACCORDING TO KREMANN AND HOFMEIER THEORY.

Ag than later when the charge is cool and approaching the eutectic curve; hence the change of composition is not along a radian, except probably just before reaching the eutectic curve. It is certain that above the melting point of zinc (419° C.) no elemental zinc can separate as a solid and it is further to be expected that only such zinc as is strongly combined with silver either as a chemical compound or stable alloy will appear in the solid that separates above say 420° C. Below this temperature, the separated solid will be progressively richer in zinc until the eutectic curve is reached. This is shown by the curved line  $a_1b$ , Fig. 3.

Another property that facilitates the action of the zinc is its tendency to replace silver, or rather Ag-Zn compounds, in solution in much the same manner as certain salts replace other salts in aqueous solutions when a large quantity of the replacing salts crystals are present. This property comes into play when removing the last of the silver. At this stage, skimming is done cold with a large excess of zinc, hence the crust is



Point	O <sub>2</sub> p.p.t. Ag	% Zn	mp °C	Zn added lb p.t.
a	200	0.000	320	—
a <sub>1</sub>	186.3	1.855	468	37.8
b	73.3	0.618	340	—
a <sub>2</sub>	22.9	2.643	396	41.6
f	<0.2	0.530	319	—
a <sub>3</sub>	256.1	2.454	481	55.9

Extracted by rich skims from a, to 420° isotherm  
107.9 oz Ag, 12.88 lb Zn pt original charge  
making 2.119 lb Zn per oz Ag in rich skims.

Extracted by 2nd skimming p† original charge  
from 420° isotherm to b, 62.8 oz Ag, 12.56 lb Zn  
from a<sub>2</sub> to f, ----- 23.1 " " 43.38 " "

Totals 919 " " 5594 " "

making 0.609 lb Zn per oz. Ag in 2nd skims  
Wt. of stubs at 20% Zn, 0.140 ton p.t. orig. chge  
Average assay of stubs, 656 oz Ag p.t.

FIG. 3.—GRAPH OF PROCEDURE OF PARKES PROCESS ZINCING, ACCORDING TO C. S. WITHERELL THEORY.

mainly composed of elemental zinc which, in contact with the molten bath, constitutes an ideal condition for the replacement action. This behavior is much favored by the steep thermal gradient downward toward the Pb-Zn line and the non-existence of a Ag-Zn binary eutectic near 100 per cent. zinc.

It is not necessary to go back to the eutectic-curve each time except the last. Point *b*, Fig. 3, is plotted on the 340° isotherm. Neither is it

necessary to raise the temperature to the melting point of the composition corresponding to the first zinc addition. An arbitrary temperature well above the melting point of zinc can be selected, for example  $450^{\circ}\text{C}.$ , and if the charge is held constant at that temperature the change of composition while adding zinc will occur along the isotherm from  $a'$  to  $a''$ , as shown in Fig. 3.

The advantage of a high temperature is quick and thorough action. The disadvantages are that it is hard on the kettle and creates oxide dross.

It is common practice at the end of the desilverization to partly freeze the Pb-Zn eutectic. The frozen mass adheres to the side of the kettle, from which it is barred loose and pushed to the center where it is hotter.

The frozen eutectic is neither a compound nor a solid solution but a mixture composed of particles of zinc included in lead; hence on heating, a liquation of the lead away from the zinc takes place and momentarily zinc is separated which, if promptly skimmed, will leave the charge with less zinc than the eutectic composition. This probably explains how the author obtained finished charges containing down to nearly 0.5 per cent. zinc.

The change of composition of the kettle charge during the second skimming is shown by the line  $a_2f$ , Fig. 3.

The important point that the author has brought out is that with any given grade of bullion a highly concentrated crust can be produced without suffering loss in precious-metal recovery, by proper addition of zinc and adjustment of temperature. The zinc, from whatever source, used for producing the skims that advance in process should be considerably limited and skimming done hot, thus causing each unit of zinc that separates from the kettle charge to carry with it a maximum amount of precious metal. The zinc deficiency is then made up in that used for the second skimmings, thus supplying for this stage an abundance of zinc, amply sufficient for complete desilverization. These latter skimmings are done while cooling down to the beginning of freezing and they produce the stubs that supply zinc to a subsequent charge.

The accompanying flow and quantity diagram, Fig. 4, will give a fair idea of what takes place in the desilverizing kettle. If all charges were alike, it would be rational to add all of the stock zinc  $Z_T$  to the second skimming, but when ascending in grade from one charge to the next the quantity  $Z_1$  must be added to the first skimming to make up the deficiency in the added stubs. It is not intended to be understood that in all cases only two skimmings are made but that all skims that advance in process are classed as first skims and the remaining skims that are reused are classed as second skims. When studying the diagram, there will be noted a marked similarity to the method known as two-stage-counter-current leaching so much used in hydrometallurgy.



GEORGE G. CRISWOLD.—Mr. Witherell's discussion brings out certain points of interest to the metallographer. The opening paragraph, though, seems a bit unfair to the lead-refinery operators. It has been most difficult to get concordant assays on the hot metal after removal of the zinc crust; and in a busy refinery the superintendent has had to play safe. It is easy to get into difficulties, as many have learned. Then, too, the influence of mass on the alloy formed has not been fully realized; in his discussion, Mr. Witherell has failed to emphasize this point which

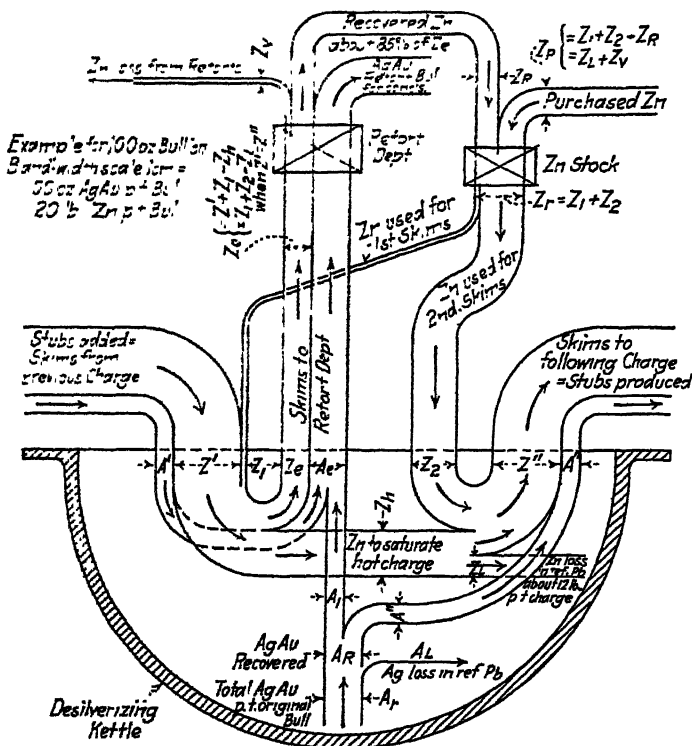


FIG. 4.—FLOW AND QUANTITY DIAGRAM OF PARKES PROCESS ZINCING FOR THE REFINING OF LEAD BULLION.

is of fundamental importance. For example, when trying out this method in one refinery, a 15-day trial was made, kettle A using the method and kettle B using the regular schedule. The charges were tapped from the same softener and thus were identical. Both were carefully cooled down to liquate out all copper possible, and pressing was done at the same temperature. In the 15 days, kettle A used 8000 lb. less zinc than kettle B but the zinc crust from kettle A was much richer in both zinc and silver than that from kettle B.

The zinc crust is, as Mr. Witherell says, a heterogeneous mixture containing gold, copper, silver, zinc, lead, arsenic, antimony, bismuth, and possibly traces of other elements. With the exception of gold and copper, which have the strongest affinity for zinc, these elements are present in the stubs. That these elements, though present in small amounts, profoundly affect the degree of concentration is probable. If arsenic and antimony are present in appreciable amounts, it is practically impossible to desilverize by means of zinc.

To give some idea of the concentration obtained, it may be stated that at one refinery the retort metal produced from 200-oz. bullion averages 5800–6000 oz. doré per ton. At another, at the time of the writer's visit, the weight of the zinc crust from 125-oz. bullion indicated

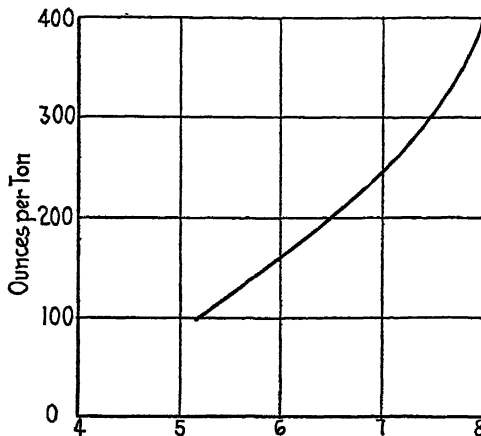


FIG. 5.—CURVE SHOWING VARIABLE FACTORS FOR CALCULATING ZINC REQUIRED IN DESILVERIZING BULLIONS OF VARIOUS GRADES.

a content of 3900 oz. doré per ton; such crust should produce a retort metal assaying 5200 oz. per ton. A third refinery was producing from 300-oz. bullion retort metal containing 6250 oz. per ton. Of course, higher concentrations can be made. There is a record of a full month's run, at a time when the refinery was not very busy and labor was plentiful and efficient, that shows a retort metal averaging 7200 oz. from bullion averaging about 250 oz. Such concentration is inadvisable in a busy refinery. It involves additional kettle work, a hot and disagreeable job at best and one little to labor's liking; it may cause irritating delays in the regular flow of operations.

The zinc for the second zining may be found as follows:

$$z = \frac{(\text{hot assay} + \text{cold assay}) \text{ tons}}{1.7}$$

when the average assay is 60. For other assays, add or subtract 1 lb. zinc for each 10 oz. silver additional or less. It would appear more logical to figure on the cold assay, but it does not work out. The important point is to get enough zinc to clean the kettle. The writer has had difficulty in cleaning the kettle when the cold assay is over 40.

At this point, it is desired to correct a statement made in the original paper in speaking of the factors, *viz.*: "That they vary . . . would doubtless be the same for all grades of bullion." This is not true. The factor is a variable, as shown by the simple curve, Fig. 5, having for ordinates the assay of the bullion, in ounces per ton. The abscissas are the factors.

The writer is quite confident, despite Mr. Witherell's doubts, that, properly supervised, the experiments as outlined would furnish valuable information. If done by students the data would probably be published.

It is probable that the percentage of zinc in the various stubs removed in the second zincing is the same. It has worked out fairly well in practice.

As to the pressing temperature, F. C. Newton<sup>4</sup> clearly shows that the maximum concentration occurs at 430° C.

To one who has carefully watched the operation, Mr. Witherell's theory on the action of zinc as a replacing agent in the second zincing seems hardly to fit the facts. As a matter of fact, the alloy that separates out in cooling down the kettle has a crystalline structure and shows a marked tendency to freeze to the sides of the kettle all the way down under the molten metal, necessitating constant scraping to insure its removal. Its action, in this respect, is similar to that of salts, which crystallize out from aqueous solutions as the density of the mother liquor increases.

Once elemental zinc has been melted down in a kettle of molten lead, it never reappears as elemental zinc, except at retorts.

The figure 0.52 per cent. zinc in the desilverized lead pumped to the refiner is a reliable one. It is the average of many assays made on samples taken over an extended period to determine the commercial feasibility of a process for recovering zinc from the desilverized lead. Samples of the molten metal, as pumped from desilverizing to refining kettle, were carefully taken.

MIL0 W. KREJCI, Orange, N. J.—The author says that the bullion should be thoroughly softened; what would he call a thoroughly soft bullion, and what would be the amount of copper and antimony?

GEORGE G. GRISWOLD.—A thoroughly softened bullion should contain not to exceed 0.06 per cent. antimony, and the arsenic should be

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<sup>4</sup>Effect of  $Zn_2Ag_2$  Upon the Desilverization of Lead. *Trans.* (1915) 51, 786.

less than 0.01 per cent. The copper may be anywhere from 0.1 per cent. down; it can be reduced to 0.05 per cent. by liquation, which should always be done.

C. S. WITHERELL, New York, N. Y.—Relative to the formula on p. 612, I cannot see how adding assays of hot and cold samples and dividing by 2 can possibly give any indication of the amount of zinc that is in the kettle charge.

GEORGE G. GRISWOLD.—The formula is empirical. The paper shows how the formula was derived. The zinc remaining in the kettle charge, after pressing, is never a constant; it was found to vary with the silver content. That is the reason why the formula gives such close results.

C. S. WITHERELL.—If that is the case, it is true through a very short range. The equation of a straight line can be taken as an empirical equation of a circle for a very short range but it would not be logical. The author's equation, as applied to the conditions of Parkes desilverizing process, must be only applicable over an extremely short range. I have tried this formula over a moderate range in a plant not far from here and it did not apply.

LAWRENCE ADDICKS, New York, N. Y.—Over what range has it been tried, over the range of the silver content?

C. S. WITHERELL.—Say, cold assay up to 100 oz. How hot did you take that hot sample, above the temperature of molten zinc, that is above 420° C. or just about 420° C.?

GEORGE G. GRISWOLD.—Just about. You are within narrow ranges when doing good work on the kettles, and the temperature will be about 420° C. The hot and cold assays will be fairly uniform from day to day regardless of the silver content of the bullion. When you talk about a cold assay of 100 oz., you are getting into work that is going to give a lot of trouble.

C. S. WITHERELL.—I know of good work that is being done with cold assay at about 75 ounces.

GEORGE G. GRISWOLD.—That would indicate good work, but not practical work when operating at capacity. With a cold assay of 100 oz., the hot assay, which is the true measure of the silver content of the kettle charge after pressing, would probably be over 200 oz., a total of 12,000 oz. is left in the kettle to be removed in the second zincing. Such work indicates a very high concentration of silver in the crust, which would probably produce a retort bullion of 8000 oz. per ton or better. It has been done over periods when tonnage of bullion was small and

retort bullion assaying 8500 oz. silver to the ton produced at times. It adds to the time and work on the kettles and was abandoned to induce our experienced kettle men remain with us. I am quite sure that a cold assay of 75 oz. will give trouble.

C. S. WITHERELL.—The only trouble, or rather difference, is more zinc is used for the second, or final, skimming and so long as this furnishes zinc for the next first-skimming no harm is done.

GEORGE G. GRISWOLD.—I have gone through that. If you have over 40 oz. you are going to have trouble.

C. S. WITHERELL.—At the plant to which I have referred the cold assay is around 55 to 65 oz. (I have since been informed that their practice is 65 to 75 oz. when treating about 200 oz. bullion.)

GEORGE G. GRISWOLD.—What is the assay of the refined lead?

C. S. WITHERELL.—Below 0.2 oz.; this means that the average is between 0.10 and 0.15 oz. per ton.

LAWRENCE ADDICKS.—You have not told us the range to which the formula has been tried; was it 100 oz. to the ton?

GEORGE G. GRISWOLD.—The formula has been tried on bullion ranging from 100 to 500 oz. per ton. It has never been tried when the cold assay of the kettle charge after pressing was over 50 oz., as it was always the aim to keep within the limits of practical work, to avoid delays that interfere with the proper sequence of operations in a busy refinery. Mr. Witherell is correct when he states that the formula is correct only over a short range; that range however, is as wide as it is safe to use with the limited kettle capacity common to most lead refineries. The cold assay will vary from 20 (it seldom goes under that figure) up to 38. You seldom get a greater variation than that.

W. F. GROSS, Maurer, N. J.—Believing that a table and chart giving the ratio pounds of zinc to ounces of silver in zinc crusts produced from various grades of bullion would be of value in connection with this paper, Mr. Alexander communicated with many refineries requesting information regarding zinc crusts obtained when doing good work. From the information submitted, Fig. 6 and the accompanying table were prepared. The data given covered bullion ranging from 25 to 500 oz. silver per ton; some refineries handling only low-grade bullion, others only fairly high-grade material. The chart and table, therefore, are a composite rather than one person's idea of what constitutes good work. Thanks are due the following for their coöperation in preparing the chart and table: E. E. Dieffenbach, of the Balbach Metals Corp.; A. F. Beasley, of the Bunker Hill & Sullivan M. & C. Co.; G. E. Johnson, of the

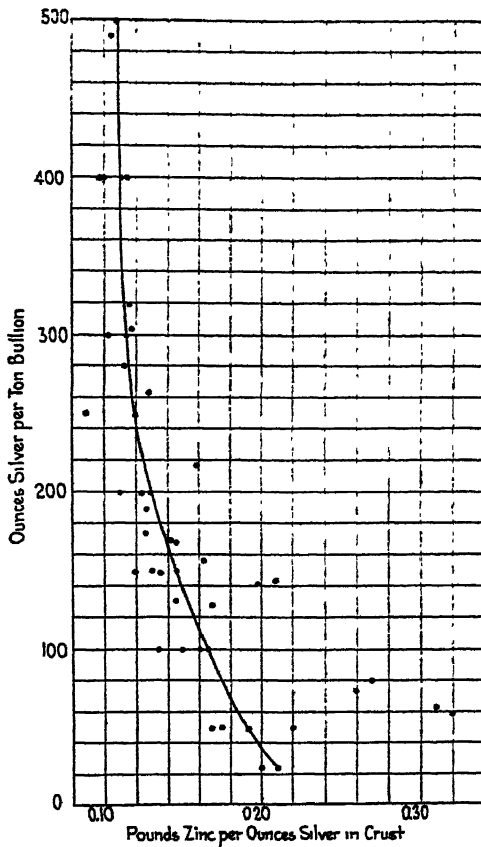


FIG. 6.

International Lead Refining Co.; A. E. Hall, of the American Smelting & Refining Co., Omaha Plant; and B. C. Stannard, of the Selby Smelting & Refining Co.

LEAD BULLION, SILVER PER TON, OUNCES	ZINC CRUSTS, POUNDS ZINC PER OUNCE OF SILVER
25	0.210
50	0.192
100	0.166
150	0.146
200	0.130
250	0.121
300	0.113
400	0.110
500	0.108

H. H. ALEXANDER, Maurer, N. J.—The theoretical curve, Fig. 6, shows what the work should be; actual practice at the various refineries

follows it closely, and were it not for some poor kettle work, the results would practically check the tables. The cold sample shows the amount of silver to be taken up by zinc, or uncombined with zinc. Kettles containing as high as 60 oz. of silver can be cleaned, but there is a possibility of extra zincing with such high assays. Possibly, by using sufficient zinc, kettles assaying much higher in silver can be desilverized with one zincing, but I doubt if it would be good practice. Theoretically, there should be little variation in the ratio of silver to zinc in the crust, and the assay of the crust would depend on the lead contents, or how well the pressing was done. If a certain amount of zinc alloys with a given amount of silver, the assay of the crust would vary with the pressure used in expelling the lead; although there is lead that cannot be removed by pressure, possibly it is combined in the alloy.

A. F. BEASLEY,\* Kellogg, Ida. (written discussion).—I believe that formulas for zincing lead bullion for desilverizing can be entirely eliminated; also the necessity of hot and cold samples by ascertaining how many ounces of silver 1 lb. of zinc will take up for any given doré content of bullion. This information is, of course, hard to obtain except over a period of a long time and it undoubtedly would have to be collected at more than one refinery.

At the Bunker Hill Smelter, our bullion runs quite uniformly for months; consequently, it is not necessary for us to watch our zincing as closely as at other plants where the doré content of the bullion is constantly changing.

During the first two or three years of the operations at the Bunker Hill, I carried on considerable experimental work trying to ascertain the best method of doing the zincing, with the idea of obtaining the highest possible concentration; the conclusion I came to, so far as our practice was concerned, was that after taking off the litharge, which formed on the lead flowing from the softening furnaces to the silver kettles, just enough zinc should be added to the bullion for saturation and stirred in thoroughly, then the stubs from the preceding kettles added, the kettle thoroughly stirred, then after the skim had risen to the surface the zinc skim pressed in the usual manner. The second addition of zinc is figured on the total zinc content of the original bullion by allowing 1 lb. of zinc for a certain number of ounces of silver. We have found that this figure changes with the doré content, or grade, of the bullion, but as we receive relatively small amounts of siliceous silver ores and as the ores smelted consist largely of Coeur d'Alene ores, our bullion has not varied in silver content to any great extent, except for a short period last summer when we received considerable high-grade silver-lead ore from the Mayo district, Yukon Territory. Next summer,

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\* Assistant Superintendent, Bunker-Hill Smelter.

when we expect to receive again this high-grade ore, we will try to make as many grades of bullion as possible and thus gather additional information with reference to the zinc and silver relationship.

We do not take hot and cold samples, as we find it is unnecessary; our lead is all of corroding quality and the silver content runs quite uniformly from 0.10 to 0.14 oz. per ton. We have found it practically impossible to get good samples of the zinc crust, so we do all of our figuring on the assays of retort products and desilverized lead. However, from such assays both the silver and zinc contents of the zinc crust can be obtained. The following figures give the results for the past two years on five grades of bullion, the concentration being figured on retort bullion content to original bullion:

PERIOD, MONTHS	ORIGINAL BULLION ASSAY, OUNCES	CONCENTRATION
5	58.04	47.22 to 1
10	63.38	43.90 to 1
4	74.10	39.10 to 1
2	80.20	39.10 to 1
2	143.00	28.4 to 1

During the period in which these figures were taken we did not get as low a copper elimination as possible, the copper assays being about 0.09 per cent., as we were short of kettle capacity. Our ratio of concentration is considerably better at the present time, as we have gotten our copper contents down to 0.06 per cent. The zinc content of the zinc crust corresponding to the figures is respectively:

	PER CENT.
1	31.20
2	30.70
3	28.10
4	30.14
5	30.70

These figures are obtained by getting the zinc content on all retort products, which is a better method than trying to obtain dependable assays on zinc crust.

Outside of the variations in the copper, arsenic, and antimony content of the crust, which should be slight on well-softened bullion, it would appear from the foregoing that the composition of our crust is only changed by the silver and lead content for any grade of bullion, that is the silver and lead replace each other.

Our zinc recovery from retorting is 89 per cent., the life of our retorts averages 70.5 heats; the average time required for retorting a 1200-lb. charge is 5.2 hr. made up of  $\frac{1}{2}$  hr. charging and pouring and 4.7 hr. to heat and complete distillation. We attribute a great deal of this success to Donaldson's condenser.



GEORGE G. GRISWOLD.—One could expect better concentration on 143-oz. bullion. Evidently too much zinc was used.

C. S. WITHERELL.—Mr. Beasley is not entirely warranted in drawing the unqualified conclusion that lead replaces silver in the kettle crust. Most of the lead present in the rich kettle crust sent to retorts is that which is physically absorbed and which pressing failed to remove. There may be present a small amount of a ternary constituent (Ag-Zn-Pb combination) as stated in my written discussion.

The first alloy to leave the molten kettle charge is high in silver and is a definite alloy. I have good reasons to believe that it is equivalent to  $\text{Ag}_2\text{Zn}_5$ ; that has not been proved except that hot skimmings (that is, skimmings produced above  $420^\circ\text{C}$ ., or above the melting point of zinc) seem to bear a ratio a little above 0.1 lb. of zinc to 1 oz. of silver, nearly the theoretical 0.104 lb. zinc per ounce of silver in  $\text{Ag}_2\text{Zn}_5$ . Below the melting point of zinc, say below  $420^\circ\text{C}$ ., instead of the separated constituent being  $\text{Ag}_2\text{Zn}_5$ , or some other stable Ag-Zn alloy, elemental zinc starts to separate or at least a constituent higher in zinc starts to separate, and the nearer you get to the eutectic temperature, about  $318^\circ\text{C}$ ., the higher will be the zinc in that separated constituent.

With low-grade bullions, 140-oz. is not very high grade but certainly 70 or 80-oz. bullion can be considered low grade, most of the separation takes place below  $420^\circ\text{C}$ ., hence the separated constituent will be rather high in zinc, much higher than say 0.11 lb. zinc per oz. of silver. If we deal with high-grade bullions, 200 or 300-oz., considerable of the separation takes place above  $420^\circ\text{C}$ ., and there will be a relatively lower amount of zinc per ounce of silver in the rich kettle crust sent to the retort department.

C. P. LINVILLE, Elizabeth, N. J.—On the chart given by Mr. Gross, so far as high-grade bullions are concerned, that is from 150-oz. up, most of the smelters reporting gave figures that are close together; but for bullion from 150-oz. down, the amount of zinc used per ounce of silver varies greatly. In some discussion, it has been stated that the amount of zinc used varied from 0.32 lb., for the lowest grade bullion, up to about 0.21 lb., for the higher grades. Some refiners are doing the same work with the same grade of bullion using from 0.17 to 0.12 lb. of zinc. That is a tremendous difference, and it would seem as if there was great need for a formula that will enable us to determine the correct amount to use, even for those low-grade bullions.

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## Efficiency of Screening

By ROBERT K. WARNER,\* E. M., NEW HAVEN, CONN.

(New York Meeting, February, 1924)

IS AN accurate measurement of the efficiency of a screen under a given set of operating conditions valuable? If so, what is the efficiency of a screen and how can it be measured? Sizing, especially of the finer sizes of material, has increased in importance in the development of flow sheets as a result of the perfecting of the rapid vibrating screens. More consideration should be given screens in the preparation of ball-mill feed, where they permit the admission of a dryer feed than the classifier. Where possible, the introduction of a screen ahead of the primary ball-mill, and the diverting of ore below, say, 4 mm. to a secondary mill, might result in a greater overall economy because of the thicker feed and the better adjustment of crushing media and mill operation to the reduction demanded. With the present trend back toward a combination of gravity methods and flotation, rather than flotation alone, the accurate, economical sizing possible with the new screens makes fine jigging a method to be considered. W. O. Borchardt<sup>1</sup> and John Bland<sup>2</sup> discuss the screening problem and also the value of close sizing in the concentration of some of the rare-metal ores.

If a screen is to be used, it should be selected in competition with others; other things being equal, that screen which makes the cleanest oversize should be preferred. The quality of the screening and the tons handled per dollar together determine the choice and, therefore, both of these must be accurately measured if a correct decision is to be reached.

Too frequently in mill design, the capacity has been considered almost to the exclusion of the completeness with which the undersize is separated from the oversize. It is, of course, possible to increase the aperture of the screen, and thus insure the removal of a sufficiently coarse

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<sup>1</sup> Estimating Screen Efficiency. *Eng. & Min. Jnl.* (1919) 107, 651.

<sup>2</sup> Notes on Screening Practice. *Eng. & Min. Jnl.* (1919) 107, 1112.

undersize, but this expedient does not affect the quality of the oversize and may cause trouble by introducing into the undersize an excess of pieces larger than those desired. Where minerals with little difference in specific gravity, but high unit value, must be separated, the quality of the sizing is by far the most important factor.

The usual method of measuring the efficiency of a screening operation is to call the percentage efficiency the percentage of the true undersize in the feed actually recovered as undersize from the screen. This calculation should be based on a screen test of the feed made on a testing sieve clothed with the same material as the mill screen being studied. The use of such a sieve will, of course, lower the apparent efficiency of any screen surface set at an angle to the horizontal but it avoids a false high efficiency due to enlarged or irregular apertures of the cloth on the mill screen being tested. The actual percentage of undersize may be determined from the mill-screen product weights or estimated from a screen test on the same testing sieve of a sample of the actual oversize.

Unfortunately for the accuracy of this method, the undersize varies widely in the readiness with which it can be separated. The same screen operated in the same way, and fed at the same rate, with two ores having the same percentage of undersize and moisture content will give widely differing "efficiencies" according as the percentage of "difficult" grains in the feed varies. The term *difficult* grains, as used here, means those grains the intermediate diameter of which approaches the width of the screen aperture. Any screen, whether it is a half-blinded fixed screen or an underloaded vibrating screen, will give practically a perfect "efficiency" calculated by the usual method on an ore, the true undersize of which is all much smaller than the screen aperture. The character of the feed often has a greater effect on the quality of the products than do the operating conditions and the type of screen. This fact causes W. O. Borchardt to conclude that it is impossible to compare the results of efficiency estimates unless the character of the feed to the screens considered is the same. He advocated the use of a factor obtained by dividing the weight of the true oversize in the feed by the weight of the actual oversize made by the screen and believes that the mathematical average of this factor and the effectiveness calculated from the undersize, as above, is the closest practical measure of screen efficiency.

The unreliability of figures based on the oversize alone is illustrated by Table 1; these results are shown also in Fig. 1. Table 1 shows the efficiencies calculated by the oversize and undersize methods of twenty-six hypothetical results on three ores. Samples of the ores, if sized on a sieve clothed with the same material as the screen being tested, would give the following results: Ore A, 10 per cent. undersize; ore B, 90 per cent. undersize; ore C, 55 per cent. undersize. It is assumed that a 100-lb. lot was screened in each test and the resulting oversize and undersize were

weighed. Variations in efficiency between different tests on the same ore were the result, therefore, of either the rate of feeding or the setting or operation of the screen. It is impossible, by the oversize method, to

TABLE 1

Screen	Weight, Pounds		Efficiency Factors	
	Oversize	Undersize	By Undersize Method $E = \frac{\text{Actual Undersize}}{\text{True Undersize}}$ Per Cent.	By Oversize Method $E = \frac{\text{True Oversize}}{\text{Actual Oversize}}$ Per Cent.
Ore A.—Test on hand sieve showed 10 per cent. undersize and 90 per cent. oversize				
a	100	0	0	90
b	98	2	20	91.8
c	96	4	40	93.7
d	94	6	60	95.8
e	92	8	80	97.8
f	90	10	100	100.0
Ore B.—Test on hand sieve showed 90 per cent. undersize and 10 per cent. oversize				
g	100	0	0	10.0
h	90	10	11.1	11.1
i	80	20	22.2	12.5
j	70	30	33.3	14.3
k	60	40	44.4	16.7
l	50	50	55.5	20.0
m	40	60	66.7	25.0
n	30	70	77.8	33.3
o	20	80	88.9	50.0
p	15	85	94.5	66.7
q	10	90	100.0	100.0
Ore C.—Test on hand sieve showed 55 per cent. undersize and 45 per cent. oversize				
r	100	0	0	45
s	95	5	9.9	47.4
t	90	10	18.2	50.0
u	80	20	36.4	56.2
v	70	30	54.5	64.3
w	60	40	72.7	75.0
x	55	45	81.8	81.8
y	50	50	90.9	90.0
z	45	55	100.0	100.0

obtain an efficiency less than the percentage of oversize in the feed. Thus, in test *a*, we get an apparent efficiency of 90 per cent., in spite of the fact that the results showed that the screen allowed no undersize to get through and was not screening at all. In test *p*, the efficiency by the oversize method was only 66.7 per cent., although 94.5 per cent. of the true undersize had managed to get through the screen. When the amounts of true undersize and true oversize are nearly equal, as in the tests on ore C, the oversize method gives results in the higher efficiencies

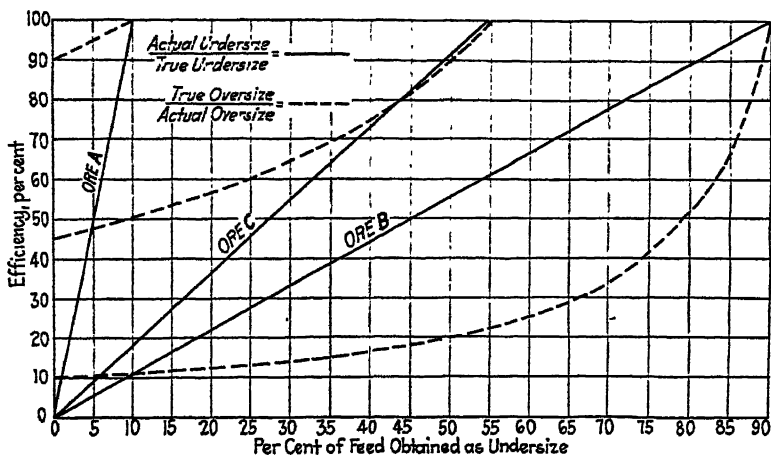


FIG. 1.

that approximate those of the undersize method but shows, as before, ridiculously high results when the screening is poor. Granting the inconsistency of the oversize efficiencies, nothing can be gained by averaging these figures with those obtained by the formula based on the undersize.

The danger in comparing efficiencies at different plants, obtained by any of these methods, is obvious, which is another reason why calculated screen efficiencies have been considered of little comparative value. How then can we obtain a measure of the quality of the work done by a screen that can safely be compared with work done on a different feed?

As any screen will pass quickly those grains in the feed that are small relative to the screen aperture, it would seem that the work done on this very fine material should not be considered in estimating screen efficiency. In short, the quality of the work done in a screening operation should be judged entirely on what happens to the difficult grains in the feed. The results then would not be obscured by the excessively fine ore present in

the feed and almost instantly removed by any screen. The proportion of difficult grains in an ore really affects the efficiency of a screen more than does the percentage of true undersize present.

The writer suggests that the best available method for estimating the quality of the work done by a screening device is as follows: Collect a sample of the feed and undersize. Size these samples on two testing sieves, the first clothed like the mill screen under investigation and the second with apertures somewhat smaller. Then the ore passing through the first sieve and held on the second will give the proportion of difficult grains, and the undersize of the second sieve plus its oversize, when divided by the total weight of the sample, will give the percentage of the true undersize present. If the weights of the mill-screen products are available, the weights of difficult grains in the feed and undersize can then be calculated. The former divided by the latter will give the screen efficiency, expressed as a decimal.

Should the weights of the mill-screen products be unknown, the efficiency can be calculated by the well-known formula for percentage extraction in concentration.

$$E = \frac{C(H - T)}{H(C - T)}$$

in which  $E$  = percentage extraction, expressed as a decimal;  $C$  = assay of concentrate;  $H$  = assay of heading;  $T$  = assay of tailing.

In applying this formula, the percentages of difficult grains in the feed and products may be substituted for the assays and the formula becomes

$$E = \frac{U(F - O)}{F(U - O)}$$

in which  $E$  = efficiency of screen expressed as a decimal;  $U$  = per cent. of difficult grains in undersize sample;  $F$  = per cent. of difficult grains in feed sample;  $O$  = per cent. of difficult grains in a sample of oversize.

A more convenient formula, as it requires the taking and screen testing of only two samples, namely the feed and oversize, may be derived as follows: In addition to the foregoing symbols, let  $A$  = per cent. of true oversize in feed sample;  $D$  = per cent. of fines (material smaller than difficult grains) in oversize sample;  $X$  = weight of feed to mill screen; and  $Z$  = weight of oversize from mill screen.

Then

$$\text{Weight of difficult grains fed to mill screen} = \frac{FX}{100}$$

$$\text{Weight of difficult grains in oversize} = \frac{OZ}{100}$$

$$\text{Weight of difficult grains in undersize} = \frac{FX}{100} - \frac{OZ}{100}$$

By definition, then

$$E = \frac{\left(\frac{FX}{100}\right) - \left(\frac{OZ}{100}\right)}{\frac{FX}{100}} = 1 - \frac{OZ}{FX}$$

$$\text{But } Z = \frac{AX}{100} + \frac{OZ}{100} + \frac{DZ}{100}$$

$$\text{Or } 100Z = AX + OZ + DZ; Z(100 - O - D) = AX$$

$$Z = \frac{AX}{100 - O - D} \quad \text{Therefore, } E = 1 - \frac{OA}{F(100 - O - D)}$$

This formula may be illustrated by the following example:

From the first line of Table 2:  $O = 100(755.0 - 21.6) \div 1937.1 = 37.86$ ;  $A = 100 - 86.55 = 13.45$ ;  $F = 100 \times 755.0 \div 2197.7 = 34.35$ ;  $D = 100(1147.1 - 239.0) \div 1937.1 = 46.88$ ; and

$$E = 1 - \frac{37.86 \times 13.45}{34.35(100 - 37.86 - 46.88)} = 1 - \frac{509.22}{524.18} = 0.0286$$

If the results are to be useful to others, standard practice must be followed in determining the limiting size of difficult grain, or this size must always be noted when the data are recorded. Opinions differ as to what the limiting size should be. Fine screening is more difficult and, therefore, generally considered less efficient than coarse sizing for many reasons. Not only must a much larger number of particles per ton of undersize be induced to pass the screen apertures, but as the difference in diameters of the largest and smallest grains is relatively small there must be, relatively, a larger proportion of grains the diameter of which closely approaches the screen aperture. The latter means a greater tendency for the screen to blind and a larger percentage of difficult grains. If only the difficult grains are considered, it will probably be found that the efficiency of a fine screen will more nearly equal that of a coarse screen operating on similarly shaped pieces.

The following example illustrates how the efficiencies calculated by the three methods compare in practice. The most convenient screen to test was a Tyler Ro-tap shaker. The results are given in Table 2. The scheme of operation was as follows. About 2200 gm. of trap rock, undersize of a 5.560-mm. sieve, was placed in a full depth 4.699-mm. sieve, the screen to be tested, and which is here called "the screen." The rock was added carefully after mixing, and the part that passed the screen while it was being filled was returned. The 4.699-mm. screen was then placed over a 3.327-mm. sieve and a pan and put in the shaking mechanism. The shaker was run for 2 sec., then the 4.699-mm. screen was carefully set aside and the machine was run long enough to divide the undersize into +3.327-mm. and -3.327-mm. products. The weights of these products are recorded in line one of Table 2. The 4-mm.

screen and contents were then returned, another 2-sec. run made, the undersize being treated as before. This series of operations was performed fourteen times in all, the running times of the machine being 2 sec., 2 sec., 4 sec., 8 sec., 16 sec., 32 sec., 1 min., 2 min., 4 min., 8 min., 16 min., 32 min., 64 min., and 128 min., respectively. Thus each run, after the first, was approximately equal in time to the sum of all the preceding ones. At the end of the last period, when the sample had been in the machine over 4 hr., it was considered completely screened and the material still on the 4.699-mm. screen was taken as true oversize.

TABLE 2.—*Material Passing 4.699-mm. Screen or Held as Oversize on Screen at the End of Interval Shown, and Efficiency of Screening at that Point, Calculated by Various Methods*

Total Time Run	Undersize					Percentage Efficiency Based on			Per Cent. Efficiency Gained per Second Based on*			
	On 3.327-mm. Grams	Through 3.327-mm. Grams	Total Grams	Oversize <sup>c</sup> Grams	Total Sample, Grams	Apparent Per Cent. Undersize	Total Undersize	Difficult Grain <sup>b</sup>	Oversize	Total Undersize	Difficult Grains	Oversize
2 sec .....	21.6	239.0	260.6	1937.1	2197.7	11.9	13.7	2.9	15.3	6.9	1.4	7.6
4 sec .....	42.6	464.0	506.6	1691.1	2197.7	23.1	26.6	5.6	17.5	6.5	1.4	1.1
8 sec .....	86.5	735.0	821.5	1376.2	2197.7	37.4	43.2	11.5	21.5	4.1	1.5	1.0
16 sec .....	202.0	1048.0	1250.0	947.7	2197.7	56.9	65.7	26.8	31.2	2.3	1.9	2.1
32 sec .....	437.1	1144.1	1631.2	566.5	2197.7	74.2	85.8	64.5	52.2	2.5	2.4	1.3
1 min .....	606.2	1147.1	1753.3	444.4	2197.7	79.8	92.2	80.3	66.5	0.20	0.49	0.45
2 min .....	659.4	1147.1	1806.5	391.2	2197.7	82.2	95.0	87.3	75.6	0.046	0.12	0.15
4 min .....	682.4	1147.1	1829.5	368.2	2197.7	83.2	96.2	90.4	80.3	0.010	0.025	0.039
8 min .....	701.5	1147.1	1848.6	349.1	2197.7	84.1	97.2	92.9	84.7	0.0041	0.010	0.018
16 min .....	714.4	1147.1	1861.5	336.2	2197.7	84.7	97.9	94.6	87.9	0.0014	0.0035	0.0068
32 min .....	724.9	1147.1	1872.0	325.7	2197.7	85.2	98.4	96.0	90.8	0.00058	0.0014	0.0030
64 min .....	738.4	1147.1	1885.5	312.2	2197.7	85.8	99.1	97.8	94.7	0.00036	0.00093	0.0015
128 min .....	747.6	1147.1	1894.7	303.0	2197.7	86.2	99.6	99.0	97.6	0.00013	0.00032	0.00076
256 min .....	755.0	1147.1	1902.1	295.6	2197.7	86.5	100.0	100.0	100.0	0.000051	0.00013	0.00032

\* Calculated by adding undersize made in each run to oversize to give oversize of preceding run; only last oversize was weighed.

<sup>b</sup> Taken in this calculation as the grains of undersize that stay on a 3.327-mm. sieve.

<sup>c</sup> The corresponding increase in efficiency divided by the time, in seconds.

In Table 2, the first line is based on the data obtained at the end of the first 2-sec. period. The figures in the other lines are obtained by adding the new undersize made in each successive run to that in the preceding line. A study of the table and the curves in Figs. 2 and 3 shows:

1. All material finer than 3.327 mm. was passed as undersize in the first minute and 91 per cent. of it in the first 16 sec. Data from a similar test showed that the through 0.833-mm. trap was almost completely



removed in 16 sec., the through 1.651-mm. in 32 sec., and the through 3.327-mm. in 1 min., as above.

2. The efficiency calculated by the oversize formula is, of necessity, distorted in the lower range because the curve has no zero point. This distortion persists in the 32-sec. point, beyond which the three curves are substantially parallel.

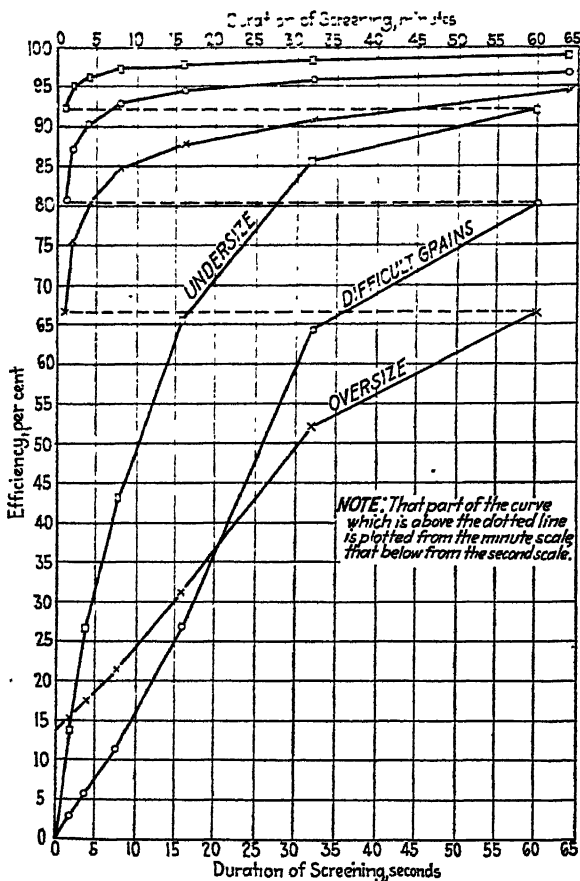


FIG. 2.

3. Except in the very low efficiencies, the curve from the difficult grains is intermediate between the other two. If the 32-sec. point on the oversize efficiency curve were connected with the zero point, instead of the 13.5 per cent. line, it would roughly coincide in its lower part with the difficult-grain curve.

4. At the beginning of the test, the ore was unstratified and, up to the point where stratification was completed, the only variable in the screening was the time. Stratification required about 32 seconds.

5. During the stratification period, it would be expected that the rate of passage of undersize, and therefore the rate of increase in efficiency, would vary directly as the time. This is markedly true in the case of the difficult-grain efficiencies, the rate of increase of efficiency per second during the first five intervals being 1.4, 1.4, 1.5, 1.9 and 2.4 per cent., respectively, thus making the time-efficiency curve substantially a straight line. It is not true of the other methods, as shown by the last three columns of Table 2.

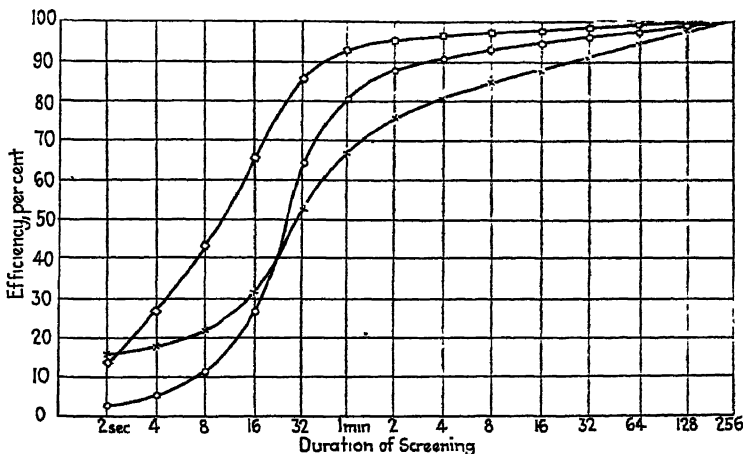


FIG. 3.—PLOTTED LOGARITHMICALLY.

6. The easy and rapid removal of the fine material causes the efficiency by the undersize method to be higher per second, especially before stratification has been completed.

7. The +3.327-mm. grains are slow in working down through the oversize, hence the increase in efficiency gained per second in the 16- and 32-sec. periods.

8. It required 21 sec. to attain a 50 per cent. efficiency by the difficult grain method as against  $10\frac{1}{2}$  and 30 sec. for the undersize and oversize methods, respectively. For a 90 per cent. efficiency, the figures were 4 min., 50 sec., and 28 min., respectively.

9. Abandoning the oversize method as hopeless, it is seen that the fines obscure and swell the efficiencies based on the total undersize. If no -3.327-mm. material had been present, the undersize efficiencies would exactly correspond with those calculated from the difficult grains. If a larger proportion of fines had been present, the early efficiencies by the undersize formula would have been larger and less consistent, than in the example considered.

The writer believes that efficiencies based on the formula

$$E \text{ per cent.} = \frac{100 \times \text{weight of difficult grains in undersize}}{\text{weight of difficult grains in feed}}$$

will so closely measure the efficiency of a screen installation that the desirability of changes can be accurately determined in advance, both from work at the plant and experience with the screen elsewhere. The interval between successive testing screens in the Tyler series should be adopted as a basis for determining the limiting size of difficult grain. Then the coarser of the two sieves used in the measurement will be clothed with the same material as the mill screen being tested and the finer sieve will be that Tyler screen having an aperture most nearly a whole interval smaller. If this practice were followed, every mill screen, regardless of its aperture, would have a definite standard range of difficult grain that would never be more than one and one-half and never less than one-half the Tyler interval. The smaller the size range accepted for the difficult grains, the more marked will be the variation of the efficiencies obtained by this method from those based on total undersize. If the lower limit is taken as zero, the efficiencies will be identical with those figured by the usual method.

## DISCUSSION

ROBERT C. CANBY, Wallingford, Conn.—On p. 632, the author speaks of the importance of using a testing sieve clothed with the same material as the screen being studied; does he regard this as essential? In practice, how does the screen efficiency calculated by the difficult-grain method compare with those computed by the usual undersize method? Is it possible by the author's method, to obtain a measure of efficiency that can safely be compared with that of another screen sizing a different ore?

ROBERT K. WARNER.—The use of a testing sieve clothed like the mill screen being studied is desirable but not essential for routine work about a mill where the character of the feed varies little, as regards the shape of the grains and the sizing test. Close agreement in size of aperture between the sieve and the screen is, however, important if the data obtained are to be valuable to others working on a different feed. If the testing sieve is coarser than the mill screen, the efficiency will appear unfairly low; whereas if it is too fine one might get efficiencies greater than 100 per cent. because of the apparent oversize in the undersize. In either of these cases the usefulness of the difficult-grain method of calculation would be reduced. As screens wear, the undersize grows appreciably coarser so that it is desirable to test screens only when the cloth is new or else to provide testing sieves that are worn about the same amount. The futility of making efficiency observations on a distorted or broken screen surface is obvious.

The effect of the application of this method of calculation will be to lower the apparent efficiencies, the variation from the undersize method

being less marked with those ores the undersize of which is relatively coarse. I do not consider this an objection; an efficiency of 80 per cent. that means something is better than one of 92 per cent. based on false premises.

The test in the latter part of the paper was repeated on each of two samples of trap rock. The percentage of true undersize was 14.3 and 12.6, respectively, as compared with 13.5 per cent. in the sample studied in the paper. The proportion of difficult grains, however, varied greatly, 67.4 and 5.51 per cent. of the feed being difficult, as compared with 34.4 in the first sample. The results of these tests were to confirm the foregoing statement.

The method described should prove an accurate guide to the adjustment of screens in a plant or to the results of competitive tests of different screens working on the same feed. If different ores are to be compared, some standard measure of the screening difficulty of each would be desirable.

Before we can safely talk about screen efficiencies or relative screen efficiencies, we must determine what a 100 per cent. efficient screen is. The definition that a screen is 100 per cent. efficient when it removes 100 per cent. of the difficult grains from the oversize may be well enough in theory but it is difficult or impossible to measure perfectly in practice. Probably the best solution is to choose arbitrarily a standard with which to compare each screen being tested; this standard might well be determined by the Milling Committee. I would suggest that a standard weight of feed, say 50 gm., times the screen aperture, in millimeters, be screened for a standard time, say 15 min., on one of the mechanical sieving machines and that the weight of difficult grains obtained in this test be used to calculate the percentage present in the feed. A weight based on the screen aperture is proposed so that the ratio between the number of grains in the sample and the number of apertures in the screen would be approximately equal and, therefore, each difficult grain would have about the same chance to get into the undersize. Any mill screen that removed as large a proportion of difficult grains as the testing sieve would then be considered 100 per cent. efficient, etc. The need for such a standard would vanish if we were sizing spheres. The shape of grains is nearly as important as the length of the intermediate diameter in determining the difficulty of screening.

W. O. BORCHERT, Austinville, Va. (written discussion).—Unless the same ore is used in each case, there is no such thing as the "efficiency" of a screening machine. The term is a misnomer and should be replaced by such an expression as "coefficient of effectiveness" or "index of performance." The author well says, "the character of the feed often has a greater effect on the quality of the products than do the operating conditions and the type of screen."

The author suggests that effectiveness of a screen should be estimated from its performance on what he well names the "difficult grains." This suggestion, while undoubtedly of value if used in connection with tests of the same or different screening machines on the same ore, does not provide that absolute means of comparison which would be essential to make possible the comparison of machines treating different ores.

The reason for this shortcoming is that he defines "difficult grains" as those the intermediate diameter of which approaches the width of the screening aperture. He does not consider the many other factors that contribute to the difficulty of causing certain grains to pass an aperture through which, theoretically, they should be capable of passing. The shape of the grains is, perhaps, the most important of these. Unfortunately for our ore-dressing practice, mineral grains are not always cubical, many grains are in the form of needles or flakes, having one or two dimensions much greater than the third. Such grains are much more difficult on certain types of screening machines than on others.

Another factor affecting the difficult grains is specific gravity. Most of the mixtures of particles that we are called upon to screen consist of several minerals of different specific gravities. Often the difficulty is enhanced because certain minerals tend to submit to or resist breaking more than others with which they are associated, or assume particularly difficult shapes upon breaking. These factors are often so marked as to cause partial concentration in screening, with, of course, a consequent distortion of the results of screen tests as compared with those made on more regular and homogeneous materials.

Even were it possible, therefore, to secure agreement on the relative size of aperture that should be used to define the difficult grains, the variability of the other factors would preclude the satisfactory comparison of the results secured with different screening machines on different ores.

The author says that I "advocated the use of a factor obtained by dividing the weight of the true oversize in the feed by the weight of the actual oversize made by the screen and believes that the mathematical average of this factor and the effectiveness calculated from the under-size, as above, is the closest practical measure of screen efficiency." This somewhat misstates my position, because it omits the condition which I imposed. What I said was: The legitimate field for the determination of screen efficiency is limited to the comparison of a given machine at different times with the same rate and quality of feed; and, if this is granted, the oversize method plotted as curve *B*, in Fig. 1, becomes the most convenient method of securing a comparative figure, because it requires the taking of but one sample, the oversize of the mill screen. This sample is screened upon a hand screen clothed with the

same screening medium as that on the mill screen, and the coefficient of effectiveness may be stated as follows:

$$C_o = \frac{\text{Oversize of hand screen}}{\text{Sample weight}}$$

I also stated that as the efficiency determined by the undersize method gives deceptive figures when the feed is low in undersize, while the efficiency determined by the oversize method gives deceptive figures when the feed is high in undersize, a mean value of the two figures might be preferable to either alone. As a matter of fact, the premise in lines *a*, *g*, and *r* of Table 1 is rather extreme, because it assumes that the screen removes no undersize whatever; this assumption results in the absurdity that the machine, by the oversize method, shows a certain efficiency without doing anything. If we take the mean of the efficiency figures of the two columns of Table I we secure the following figures.

SCREEN	$\frac{E_u + E_o}{2}$	SCREEN	$\frac{E_u + E_o}{2}$	SCREEN	$\frac{E_u + E_o}{2}$
a.....	45.00	j.....	23.80	s.....	28.65
b.....	55.90	k.....	30.55	t.....	34.10
c.....	66.85	l.....	37.75	u.....	46.30
d.....	77.90	m.....	45.85	v.....	59.40
e.....	88.90	n.....	55.55	w.....	73.85
f.....	100.00	o.....	69.45	x.....	81.80
g.....	5.00	p.....	80.60	y.....	90.45
h.....	11.10	q.....	100.00	z.....	100.00
i.....	17.35	r.....	22.50		

If these values are plotted in Fig. 1 for the corresponding ores, they will give curves lying intermediate between the undersize and oversize "efficiency" curves in each case, and as the author says, "3. Except in the very low efficiencies, the curve from the difficult grains is intermediate between the other two." That this is true, at least in the example given in Table 2, is shown by comparing the means of his efficiencies based on undersize ( $E_u$ ) and average ( $E_o$ ) with the efficiencies based upon difficult grains ( $E_d$ ).

$E_u$	$\frac{E_u + E_o}{2}$	$E_o$	$\frac{E_u + E_o}{2}$
2.9	14.50	90.4	88.25
5.6	22.10	92.9	90.95
11.5	32.35	94.6	92.90
26.8	48.45	96.0	94.60
64.5	69.00	97.8	96.90
80.3	79.35	99.0	98.60
87.3	85.30	100.0	100.00

Another factor, not discussed by the author, that would affect the results obtainable by his method of estimating efficiency of screening on the basis of the difficult grains, is the relative quantity of grains a

little larger than his screen aperture, and a little smaller than his limiting size for defining the difficult grains. As I have pointed out elsewhere, the direct cumulative plot of a screen analysis of an ore rarely gives a straight line; the curves generally show marked, often for a given ore, characteristic "bunching." Some ores give convex, some concave, and some reverse curves, while two with which I am familiar almost always show a decided cusp, which seems to represent the point at which the crystals of the major mineral are free.

I am afraid that all this does not get us very far, although the object sought is worthwhile. Perhaps we may be driven to standardizing the efficiency tests of screens with some uniform and readily procurable sand, much as Ottawa sand has been adopted as the standard with which to mix cement in making mortars and testing machine briquets, but, even if we did, we would learn little or nothing about the performance to be expected of the machine in working upon ores. Consider, for example, the futility of testing a screening machine with a granular standard sand and trying to figure from that what it would do on an ore consisting of a mixture of pyrrhotite, quartz, and mica.

V. E. FLANAGAN,\* Fort Wayne, Ind. (written discussion).—In this paper, consideration is given the fact that a screen set on an angle normally shows a lower apparent efficiency. In most operations this is taken care of by the use of Ton-Cap or Rec-Tang screen cloth. No mention is made, however, of the fact that in a rapidly vibrating screen, such as the Hum-Mer or the Leahy No-Blind, the effective diameter of the wires in the screen cloth is greater than the actual diameter. This fact is apparent when one observes the operation of one of these screens without load.

To obtain an undersize product of a certain mesh, a screen cloth with a larger clear opening is employed; with vibrating screens of proper design an undersize product is obtained that contains no particles larger than the desired mesh, even though the actual opening of the screen cloth is somewhat larger.

If the formula proposed in this paper were accepted, a vibrating screen equipped with a 10-mesh screen cloth that might be producing a very acceptable 12-mesh product would be rated at a much lower efficiency than a horizontal shaker screen equipped with a 12-mesh screen cloth and producing the same quantity of undersize, treating the same feed. It does not seem fair to consider a universal efficiency formula that would show one screen to a disadvantage, even though it were doing equal, or better, work.

In the Pennsylvania anthracite region, the standards for the various sizes are based on round holes in punched plate. I believe there is a place for the vibrating screen in the preparation of the finer sizes of

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anthracite. Much experimenting will have to be done to adapt the vibrating screen to this work in order to determine the proper slopes and the proper mesh of screen cloth for the vibrating screen to produce products that will correspond to the present standard.

From an operating point of view, screening is an operation to remove particles smaller than a certain size. These particles are known as "undersize" and if all the undersize in the feed is removed by screening 100 per cent. efficiency has been achieved. Several factors affect this operation. Among these are the size at which screening is desired, the moisture content of the feed, and the presence of difficult grains. The most important factor, when considering the results to be obtained in screening an ore, is the character of the ore; the presence of difficult grains is entirely dependent on the character of the ore considered.

In every grinding, crushing, concentrating, or other milling problem, a certain result can be accomplished, and if accomplished, a maximum efficiency is obtained. In every case, the most efficient result is entirely dependent on the character of the ore. It is, therefore, hard to imagine a universal formula for any of these operations, the expression of which in percentages would give a fair comparison between similar operations on different materials. A 75 per cent. efficiency for an operation in a certain mill may represent results equally as good as an efficiency of 85 per cent. for the same operation in another mill treating different material.

In an early paragraph in the paper, reference is made to an underloaded vibrating screen giving practically perfect "efficiency," calculated by the usual method on an ore. It has been my experience that a vibrating screen does not give as high an efficiency when underloaded as it does when fully loaded and fed with a uniform feed.

A consideration that ordinarily is not given enough attention when considering a screen is the degradation in the material handled that results from the use of certain types of screening equipment. I have samples of ore passed through a certain size mesh by two screening methods. We will assume that each of these samples had been crushed and eventually screened through a 10-mesh screen. In this particular case, the zinc content of the original ore was 17 per cent. One sample of —10-mesh material analyzed, we will say, 16.5 per cent. zinc while the second sample of —10-mesh material analyzed only 12 per cent. zinc. The particles that make up the second sample have the appearance of river sand, as they were rolled in the screening process, and a part of the zinc, being softer than the gangue, passed on as slimes. The first sample has very distinct sharp corners; and while it was screened to pass the same mesh as the second sample, very little degradation took place in the screening process. This matter of degradation in various screening methods would warrant research, and the results from such research would be valuable to the mining industry.



ROBERT K. WARNER (author's reply to discussion).—In replying to the discussion, let me first disclaim any intention of proposing to make screening an exact science. If by any means we are able to measure accurately the efficiency of a screen or the most efficient way of operating a screen for a given service, we have only partly solved the problem; the final choice depends on a compromise between the efficiency and the capacity per dollar of capital and operating cost.

If we follow Mr. Borchardt, and limit the consideration of efficiency to the study of a "given machine, at different times with the same rate and quality of feed," the measurement would be valueless because the variation would only show lack of uniformity in taking and testing the samples. Since, as Mr. Borchardt himself agrees, efficiencies based either on the oversize or the undersize are deceptive when the proportion of oversize or undersize respectively is large, why hope to improve matters by averaging? My contention is that the real measure of the ability of a screen is the completeness with which it places the difficult grains where they belong. If we can determine the input of these grains as feed and the output as undersize, we have a measure of the quality of the operation, whether it is called efficiency or by some other name.

Mr. Flanagan's protest against using sieves clothed like the screens, in comparing vibrating and shaking screens making the same sized undersize, is a just one. Taking the condition he mentions, let it be assumed that the object of the sizing is to make a 12-mesh product, or to leave a minimum amount of 12-mesh material in the oversize. The upper limit of the difficult grains would then be the aperture of a 12-mesh sieve for both screens. If material coarser than 12-mesh was objectionable in the undersize, it would be necessary to take a sample of the undersize and either neglect this too coarse material or penalize the screen if any was found. As will be seen from my answer to Mr. Canby's third question, I believe that an empirical standard of the difficulty of screening a given feed can be set up and that this, by permitting a commercially accurate comparison, would avoid the difficulty mentioned by Mr. Flanagan. In using the term "underloaded vibrating screen" on p. 632, I meant one that was operated so as to give the maximum quality in the products even at a sacrifice of capacity.

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## Surface Reactions in Flotation

BY A. W. FAHRENWALD, E. M., MET. EN.,\* MOSCOW, IDAHO

(New York Meeting, February, 1924)

### SURFACE REACTIONS WITH SPECIAL REFERENCE TO THE AIR-LIQUID INTERFACE

THE physics and chemistry of the flotation process are not well understood. Many papers dealing with the theory of flotation have been published but most have been narrow in their viewpoint. No theory advanced has done more than explain, more or less satisfactorily, various isolated phenomena. Scientists have done little with the problem, doubtless because they have not seen sufficient of the practical side of the subject to have their interest aroused. Any attempt to explain the mechanism of flotation that considers only contact angles, surface tension, adsorption, the floating of needles, flocculation, or any other single and narrow phase of the question is sure to be disappointing. Flotation is a problem of colloid chemistry and must be studied as such.

In a broad general way, flotation is a process involving and operating by virtue of surface reactions. The term "surface reactions" may be open to criticisms. Many chemists give the term "reactions" a definite and restricted meaning and to such the term may connote change in atomic grouping in strict stoichiometric ratios. While Langmuir looks upon adsorption as a reaction, and there is much evidence in support of this view, we may look on adsorption as a physical process as far as this paper is concerned. The term seems well suited to the work in general. Presumably these reactions are reactions between the same kinds of forces (electrical) and differ only in degree and in the surface manifestations produced. This premise seems logical if we accept the theory that the atoms of all elements are made up of grains of electricity, having mass and charge, called electrons; and that atoms differ from one another only in the number and arrangement of the electrons about a positive nuclear

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charge. Certainly, if the surface reactions are not directly between atoms or electrons, the energy possessed by these ultimate particles is the seat of, at least, many of the phenomena in flotation. In any serious study of the theory of flotation, the modern theories of the structure of matter must be reckoned with.

Frequently, in this paper, substances will be spoken of as polar and non-polar, G. N. Lewis<sup>1</sup> would classify substances as polar and non-polar, rather than inorganic and organic. A *non-polar molecule* is one in which the electrons belonging to the individual atom are held by such restraints that they do not move far from their normal positions; while in the *polar molecules* the electrons, being more mobile, so move as to separate the molecule into positive and negative parts. In an extremely polar molecule, such as sodium chloride, it is considered probable that in most of the molecules the chlorine atom has acquired a unit negative charge and therefore the sodium atom has a unit positive charge. The process of ionization is thought to consist only in a further separation of these charged parts. According to Latimer and Rodebush,<sup>2</sup> all the inter-medial stages between polar and non-polar compounds doubtless occur, depending on the extent to which the neutrality of the molecule is disturbed, as the electron is more or less completely displaced from one atom to the other.

Non-polar substances do not react with water to any appreciable extent. Flotation oils are both polar and non-polar; *i.e.*, the molecules are composed of non-polar groups, such as the methyl, CH<sub>3</sub>, group, united with polar groups, such as the hydroxyl, OH, group, in the alcohols and the carboxyl, COOH, group in the fatty acids. The spreading of such a substance is due to the polar, or soluble, group in the molecules.

The importance of the newer ideas as to the shapes and structure of molecules can scarcely be overestimated. Such phenomena as surface tension, contact potential, and emulsification have taken on a new significance in the light of the recent theories of atomic and molecular structure. In this paper, and others to follow, the effort is made to thrash out the matter of surface reactions and the part played by them in flotation.

### SURFACE TENSION OF LIQUIDS

Langmuir<sup>3</sup> has shown that the surface tension of a liquid is not a property of the molecule as a whole or of the group molecules, but depends

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<sup>1</sup> *Jnl. Am. Chem. Soc.* (1916) 38, 762.

<sup>2</sup> *Jnl. Am. Chem. Soc.* (1920) 42, 1419.

<sup>3</sup> *The Constitution and Fundamental Properties of Solids and Liquids. Jnl. m. Chem. Soc.* (1917) 39, 1349; also *Chem. & Met. Eng.* (1916) 15, 468.

only on the least active portions of the molecules and on the manner in which they are able to arrange themselves in the surface layer. The idea is best brought out by quoting from Langmuir's paper: "According to this theory, the group molecules of organic liquids arrange themselves in the surface layer in such a way that their active portions are drawn inward, leaving the least active portion of the molecule to form the surface layer. By 'active portion' of a molecule is meant a portion which is characterized by a strong stray field (residual valence). Chemical action may be assumed to be due to the presence of electromagnetic fields surrounding atoms. Surface tension (or surface energy) is thus a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms. The molecules in the surface layer of the liquid arrange themselves so that this stray field is a minimum." A similar theory was developed independently by Harkins.<sup>4</sup>

Langmuir has calculated the dimensions of molecules of a number of substances of interest in flotation. His figures, given in Table 1, help us to gain a conception of the size and shape of the things with which we are working.

TABLE 1.—*Size of Molecules*

Substance	Formula	Cross Section, Square Centimeters	Length, Centimeters
Palmitic acid.....	$C_{16}H_{31}COOH$	$21 \times 10^{-16}$	$24.0 \times 10^{-8}$
Stearic acid.....	$C_{17}H_{33}COOH$	$22 \times 10^{-16}$	$25.0 \times 10^{-8}$
Cerotic acid.....	$C_{23}H_{45}COOH$	$25 \times 10^{-16}$	$31.0 \times 10^{-8}$
Tristearin acid.....	$(C_{17}H_{33}O_2)_3C_3H_7$	$66 \times 10^{-16}$	$25.0 \times 10^{-8}$
Oleic acid.....	$C_{17}H_{33}COOH$	$46 \times 10^{-16}$	$11.2 \times 10^{-8}$
Triolein.....	$(C_{18}H_{33}O_2)_3C_3H_7$	$126 \times 10^{-16}$	$18.0 \times 10^{-8}$
Trieloiden.....	$C_{18}H_{33}O_2C_3H_7$	$120 \times 10^{-16}$	$18.6 \times 10^{-8}$
Cetyl palmitate.....	$C_{16}H_{31}COOC_{16}H_{33}$	$23 \times 10^{-16}$	$41.0 \times 10^{-8}$
Myricyl alcohol.....	$C_{10}H_{21}OH$	$27 \times 10^{-16}$	$41.0 \times 10^{-8}$

#### METHODS USED IN MEASURING SURFACE TENSIONS

A film method<sup>5</sup> of measuring the surface tension was used in this investigation. The drop-weight and the Jaeger capillary-bubble methods

<sup>4</sup> *Jnl. Am. Chem. Soc.* (1917) 39, 541.

<sup>5</sup> A. W. Fahrenwald: The Film Method of Measuring Surface and Interfacial Tension. *Jnl. Am. Optical Soc. and Rev. of Sci. Instruments* (Sept., 1922). A. W. Fahrenwald: Surface Energy and Adsorption in Flotation. *Min. & Sc. Pr.* (1921) 123, 227.

were also used to check certain points, but not in the regular work as they are not well adapted to the study of surface tension as influenced by time. The film method, using the automatic gravity balance, is easily sensitive to 0.1 dyne and measurements on a surface that has an invariable tension are reproducible to within approximately 0.5 per cent.

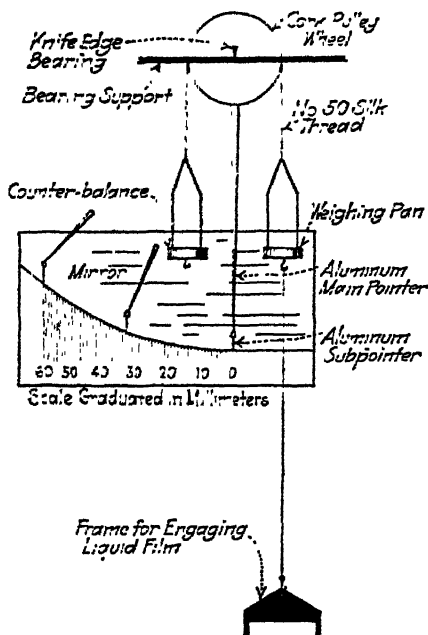


FIG. 1.—SURFACE-TENSION MEASURING INSTRUMENT.

Since this work was done, Taggart and Gaudin<sup>6</sup> have published the results of a research on certain phases of the theory of flotation closely related to the ones reported here and performed with the Fahrenwald type of surface-tension measuring apparatus. Frequent reference to their work will be made. The latest set-up for making measurements with this instrument is shown in Fig. 1. The improvements over the instrument shown and described in the foregoing references are:

1. The scale and swinging member, or balance, are a unit and are not connected, in any way, to the mechanism for raising and lowering the dish containing the liquid under investigation; this prevents jarring and harmful vibration of the balance.

<sup>6</sup> Surface Tension and Adsorption Phenomena in Flotation. *Trans.* (1923) 68, 479.

2. A mirror is attached to the scale, or dial, back of the pointer; by lining up the pointer with its image in the mirror, the observer can make readings when his eye is normal to the scale. This has proved to be an important refinement.

3. An aluminum subpointer about  $\frac{5}{8}$  in. long, swinging in a loop on the end of the main aluminum pointer, hangs vertically at all positions of the main pointer. Its lower end is flattened to nearly a knife edge, which gives it a mere hair-line appearance against the graduated scale, which is ordinary cross-section paper of millimeter squares.

4. The mechanism for raising and lowering the dish, to contain the liquid to be tested, is shown in Fig. 2. It is easily constructed and is a most flexible

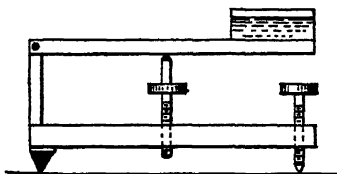


FIG. 2.—MECHANISM FOR RAISING AND LOWERING SURFACE-TENSION DISH.

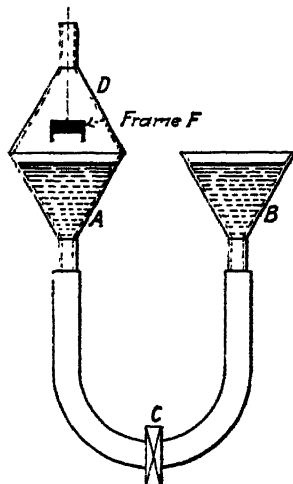


FIG. 3.—FUNNEL SET-UP FOR CONTRACTION AND EXPANSION EXPERIMENTS.

device in all kinds of experiments. The table on which the dish rests is raised or lowered by either thumb wheel; in certain measurements both wheels are used. The device is particularly convenient in that ring stands, etc., can be set upon the table and horizontal shifting of the dish is avoided.

5. When measurements on covered surfaces are desired or when it is desired to determine the effect of compression and expansion on the value of surface tension, the funnel set-up shown in Fig. 3 is convenient. There are other apparatus that may be used for this purpose.

The bases of the funnels are ground to give a perfect fit when put together as shown. Funnel B serves as a reservoir for the liquid to be tested. The principal features of this set-up are: (1) The tension in a relatively fresh or a continuously expanding surface may be measured. The procedure is as follows: Raise funnel B sufficiently above funnel A so that when the valve C is opened funnel B will drain completely into funnel A. Regulate by means of the valve C so that the liquid level in funnel A will rise at a convenient rate. Funnel A should then be raised until the liquid surface engages the film-forming frame F, then lowered to form the film. (2) The inverted funnel D prevents contamination of

the liquid surface and provides an atmosphere above the surface that is saturated with the vapor of the liquid. When volatile substances are being worked with, evaporation is reduced to a minimum. (3) The effect of compression on the surface tension of a liquid surface may be conveniently investigated as follows: All of the liquid should be allowed to flow rapidly from funnel *B* into funnel *A* and the tension of the fresh surface measured. Funnel *B* should now be dropped considerably below funnel *A* and the valve *C* carefully opened to effect a lowering of the liquid surface in the funnel. By this procedure, a surface may be shrunk from 100 per cent. into an area of 5 per cent. This method offers less chance of surface contamination, through manipulation and other sources, than the open-trough method used by Devaux and Langmuir, and which is also used in some of the following experiments. When carrying out an experiment, the inside of funnel *A* should be coated with paraffin wax, otherwise the surface film will not be compressed as the liquid level drops, for a film of the liquid remains on the side of the funnel on which the contaminant spreads.

#### THE WATER-AIR INTERFACE

The most generally accepted value for the surface tension of pure water is 72.8 dynes per cm. at 20° C., which was determined by Harkins and Brown.<sup>7</sup> Practically the same value has been obtained by the author<sup>8</sup> using the film method. This constant has been determined by hundreds of other experimenters, and all known methods have been used; many of the best determinations are very close to the value given above, but many place it between this value and 81 dynes per cm. at the same temperatures.

A large number of factors may affect the surface tension of water, as will be evident as we analyze the subject.

#### EFFECT OF GASES ON THE SURFACE TENSION OF WATER

It has been shown by Ferguson,<sup>9</sup> Bhatnagar<sup>10</sup> and Richards and Carver<sup>11</sup> that the surface tension of water is less when in contact with gases than when in contact with air or its own vapor. Their figures are tabulated in Table 2.

Richards and Carver found that with such substances as benzene, toluene, ether, etc., there was also a slight increase in surface tension

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<sup>7</sup> *Jnl. Am. Chem. Soc.* (1919) 41, 499.

<sup>8</sup> *Min. & Sc. Pr.* (1921) 123, 227.

<sup>9</sup> *Phil. Mag.* (1914) 28, vi; 403.

<sup>10</sup> *Jnl. Phy. Chem.* (1921) 29, 716.

<sup>11</sup> *Jnl. Am. Chem. Soc.* (1921) 43, 827.

TABLE 2.—*Effect of Gases on Surface Tension of Water*

Contact Surface	Observer		
	Ferguson at 15° C.	Bhatnagar at 15° C.	Richards and Carver at 20° C.
Water-vacuum.....	.....	71 30	72 75
Water-hydrogen.....	.....	72.83	
Water-nitrogen.....	.....	73 00	
Water-carbon monoxide .....	.....	73.00	
Water-carbon dioxide. ....	73.04	72.85	
Water-air.....	73.83	73 10	72.73

when air was removed. Bhatnagar's figures show a slight increase in the tension in the same order as the densities of the gases, except for carbon dioxide, the solubility of which in water, it is thought, may be connected with this result. But the difference here is, in any case, so small as to have no material effect in flotation, though the differences and causes are not insignificant or negligible when the method of studying the theory of the process is based on surface-tension measurements.

Richards and Carver, using the capillary rise method, find only a slight difference, 0.02 dyne, in air and in vacuum, while Bhatnagar, using the sphere-segment method of Ferguson, records a difference of 1.8 dyne; the former observers find the surface tension greater in the absence of air while the latter finds the greater value in air.

Ferguson, using Jaeger's capillary-bubble method, found the surface tension of water to be 0.79 dyne greater in air than in an atmosphere of carbon dioxide, while Bhatnagar's figures show a difference of only 0.25 dyne. The results are noticeably contradictory although each observer took every possible precaution.

#### SURFACE TENSION OF WATER AND THE TIME FACTOR

Ordinary laboratory distilled water is never entirely free from impurities. Bhatnagar found that a sample of laboratory distilled water redistilled through a Liebig's condenser contained noticeable amounts of silicates and ammonia, but he was able to get water free from volatile nitrogenous organic compounds by redistilling water to which potassium permanganate and caustic soda had been added, and silicates could be avoided by using a tin condenser. It might also be pointed out that laboratory distilled water is never neutral, but ranges in pH\* value from

\* pH has reference to the acidity and alkalinity of the solution. A solution having a pH value of 7 is neutral; a solution having a greater pH value is alkaline, one with smaller pH value is acid. The significance of pH is defined later.



5.5 to 6.0. Tap water at Moscow, Idaho, is more nearly neutral at all times.

By using the film method, the tension in a water surface of practically any age greater than about 30 sec. can be determined. The newest surface that can be measured is that of a continuously expanding surface, as effected by using the funnel set-up shown; in this case, the age of the surface is much less than 30 sec. and the measurement closely approximates the dynamic surface tension.

A rather large number of experiments were made on water to determine the relation, if any existed, of the age of the surface to the value of the surface tension. One series of tests is given in Table 3. In this series, the plate was suspended in the liquid during the standing period and, in reality, a fresher surface was produced when the plate was withdrawn than if the dry plate had just touched the surface and the film formed, as was done in previous experiments which showed a drop in surface tension with time.

TABLE 3.—*Variation in Surface Tension of Distilled Water with Age*

Container	Age of Surface	Surface Tension at Observation Temperature	Surface Tension at 20° C.
Pyrex funnel.....	Expanding	72.8 at 25° C.	73.0
Pyrex beaker.....	18 hr.	72.2 at 25° C.	72.9
Petre dish.....	18 hr.	72.2 at 25° C.	72.9
Paraffined beaker.....	18 hr.	72.2 at 25° C.	72.9
Pyrex funnel.....	Expanding	73.0 at 19.5° C.	72.8
Pyrex funnel.....	24 hr.	73.5 at 16.1° C.	72.8

While the results in Table 3 show no significant change in the surface tension of laboratory distilled water, with age, occasional samples handled with the utmost care showed a drop of 1 or 2 dynes when they had stood over night. The samples of Table 3 were covered at all times; the only opening to the water surface was that in the stem of the upper funnel through which the thread, supporting the film-forming frame, passed. The measurements were then presumably made on surfaces in contact with an atmosphere saturated with water vapor.

Then, as far as the film method is concerned, as it is sensitive to  $\pm 0.1$  dyne, there is no change in the surface tension of water free from contaminants, although a method sensitive to the second decimal place might show a drop. Later compression experiments on aged surfaces indicated the presence, in the water surface, of a surface-tension-lowering constituent.

The tension curve of the 24-hr. surface of Table 3 when compressed, by allowing the water to run slowly back into the reservoir funnel, pointed downward when the compressed surface was 25 per cent. of the original and went as low as 35 dynes at the end of the compression. The tension in the compressed surface increases slowly if allowed to stand undisturbed, but does not go back to normal. If the surface is again

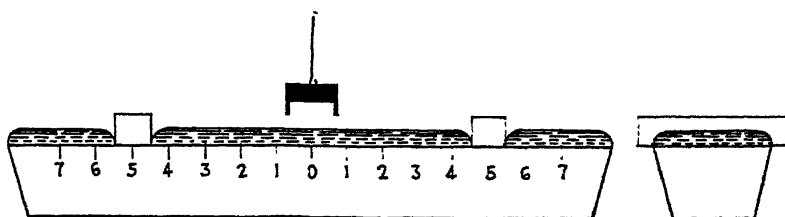


FIG. 4.—TROUGH USED IN COMPRESSION EXPERIMENTS.

expanded, the tension goes back to normal; also, if the compressed area is agitated, the tension goes back to normal.

Using a shallow paraffined trough 3 in. wide by 16 in. long, which can be filled with water to  $\frac{1}{16}$  in. or more above the surface of the pan without overflowing, and a couple of paraffin blocks, Fig. 4, compression experiments were made on tap water with the results shown in Table 4.

TABLE 4.—*Effect of Compression on Surface Tension of Tap Water at 21.4° C.*

Age of Surface, Minutes	Area Surface, Square Inches	Per Cent. Original Surface	Surface Tension
2	48	100.0	73.5
4	42	87.5	73.4
6	36	75.0	73.4
8	30	62.5	73.3
10	24	50.0	73.2
12	18	37.5	73.2
14	12	25.0	66.0
16	6	12.5	47.0

That there is a slow surface concentration process of some substance in the water surface is clearly shown. This can be demonstrated nicely by compressing surfaces of increasing age. A freshly skimmed surface of ordinary distilled water that had stood in a carboy for several days showed no drop in tension when contracted into 1 per cent. of the original surface. Surfaces 4, 6, 10, and 12 min. old began to drop in tension at compressions equal to 3, 4, 8, and 10 per cent. of the original surface.

Compression experiments similar to the foregoing were carried out in paraffined and unparaffined funnels, both covered and uncovered, with comparable results. Duplicate experiments were made in a 5-in. porcelain evaporating dish with the object of eliminating the question of contamination from the rubber tube connecting the reservoir and the paraffined funnel. The liquid surface was expanded and contracted by adding or withdrawing water by means of a pipette; this method gave similar results.

Later tests on salt solutions showed an apparent concentration of hydroxyl ion, OH, in the surface. The surfaces of several samples of water, both distilled and tap, were skimmed and the pH value of the skimmings and of the residual water were determined by the colorimetric method. Several methods of obtaining a sample (about 20 c.c.) of surface water were used, but the one giving the most noticeable difference in color of skimmings over original solution, when the indicator was added, was to place about 200 c.c. of water in a large crystallization dish, then siphoning out all but enough for a test. The rate of siphoning should be slow, 30 to 40 drops per minute. The pH value of the distilled water used was between 5.7 and 6.2 and the skimmings from various samples went from a just faintly noticeable difference in intensity of color to as much as 0.6 pH.

Doctor Eastman, of the chemistry department of the University of California, suggested that it may be a case of negative adsorption of carbonic acid, the carbonic acid being due to dissolved carbon dioxide from the air. To check up this point, samples of distilled water were boiled, to expel all dissolved gases, and cooled out of contact with air. Skimming tests were made on these samples as soon as they were cool. No noticeable difference in pH value of skimmings and residual water could be detected by the use of brom-cresol-purple indicator. The same sample of water standing in an Erlenmeyer flask for a couple of hours, subjected to the skimming test, showed a noticeable increase in alkalinity over that of the volume of the water. Distilled water saturated with carbon dioxide had a pH value of approximately 4.5; the skimmings from this solution were approximately 5.4 pH. While both are acid, the surface water is considerably less acid than the interior water. These experiments point pretty clearly to  $\text{CO}_2$  as the disturbing factor. An attempt was made to check the results by the use of the hydrogen electrode, but it was impossible to obtain steady and unchanging electromotive forces. The electromotive force would quite quickly reach an indefinite maximum and then slowly drop with time as the hydrogen bubbles passed through the solution under examination. The reason for the failure of the hydrogen electrode to work satisfactorily on these solutions was not found as time for further experiments was not available.

The difference in the pH value of the surface water and the interior water of the same sample is, as far as the writer knows, a new observation and apparently one of some significance. It is quite possible that there is some relation between the observed difference in acidity in the surface layers and the interior portions of water and the tendency of the surface tension of such solutions to drop with age.

N. K. Adam<sup>12</sup> states that "Perfectly clean water surfaces were not obtained: on the cleanest the float would move away from the barrier at 0.5 cm., with a weight in the balance pan of 0.05 gm. . . . A clean atmosphere is essential for these experiments." He was making experiments on water preliminary to compression experiments on palmitic-acid films on water, using a method similar to that used by Langmuir. Another interesting point recorded by him is the difference in the compression curves on a fresh and on an aged water surface, for which he is unable to account. It may be suggested that this difference is due to the difference in the pH value of old and fresh surfaces of water.

Experiments show that for all intents and purposes the surface tension of water does not vary with the age of the surface, if certain precautions are taken. Unusual care, however, must be taken to prevent surface contamination. Reliable results cannot be obtained if one works near chemical laboratories or in laboratories containing volatile contaminants such as oils. On warm days, vapors from the body of the experimenter are possible contaminants. By the film method, the plate should be immersed considerably below the surface film.

#### SURFACE TENSION OF FLOTATION OIL-WATER MIXTURES

The only organic substances that have been found of practical use in flotation are those that lower the surface tension of water. Distillation products of wood (hard and soft) and coal tar have held the field. It is highly important that something of the exact effect of these substances on the surface energy of water should be known. Mixtures of flotation oils and water will here be referred to as "emulsions," disregarding for the time the question of the actual condition of the oil in the water.

The first experiments on the surface tension of flotation oil-water emulsions and on the adsorption of the oils from water by minerals were made over three years ago. Principles of the methods used in the investigation, with some of the data obtained, have been published.<sup>13</sup>

Before adsorption data of any degree of accuracy could be obtained, it was necessary to work out reliable methods of measuring the surface tension of the liquids on which adsorption tests were to be made. The

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<sup>12</sup> The Properties and Molecular Structure of Thin Films of Palmitic Acid on Water. *Proc. Roy. Soc., London* (1921) 99A, I, 330.

<sup>13</sup> *Min. & Sc. Pr.* (1921) 123, 227.

liquids included emulsions and true solutions. Very few data, if any, bearing directly on this subject have been published, with the exception of some work of Lord Raleigh, Freundlich, Milner, and a few others who have recognized the variability of surface tension of such liquids with time.

The first attempts at measuring the surface tension, of both emulsions and true solutions, by the film method indicated several difficulties. For example, if 1 liter of an emulsion of a pine oil was made up by shaking the oil and water vigorously in a 2-liter acid bottle, it was impossible to take from this mixture, by means of a pipette, two or more portions and obtain concordant values for their surface tensions. The difference was often as much as several dynes. All attempts to standardize a procedure for making up the emulsion and placing it in the dish for measurement failed to give satisfactory results.

#### SURFACE TENSION OF EMULSIONS AND THE TIME FACTOR

It was observed that usually the tension dropped with the age of the surface and also that, with the higher concentrations (with this particular pine oil, above 20 mg. in 100 c.c. of water) a film of the oil would slowly form on the surface of the emulsion. The formation of this surface film was, at first, thought to be the factor causing the irregular and inconsistent results, but visible surface films do not form in the case of very low concentrations; such films appear only when the concentration of oil in water is relatively high. It was found that the factor giving the trouble in the low concentrations worked with was not the surface film but the age of the surface, temperature and other conditions being constant.

To investigate the question of the age of the surface of these emulsions and its effect on surface tension, the following experiments were made: An emulsion containing 10.1 mg. of a pine-tar oil in 100 c.c. of distilled water was made up. A part of it was removed from the flask with a pipette and introduced into a shallow crystallization dish, such as is used in bacteriological laboratories. The dish was filled until the liquid came slightly above the rim and the surface skimmed several times with a strip of paraffined paper. This treatment brought the surface tension up to 72 dynes. Without disturbing the surface any more than necessary, surface-tension measurements were made at intervals of 1 min. The results of the experiment are shown in curve A, Fig. 5.

As there is a gradual drop in surface tension with age of surface, it was thought that if an equilibrium point for this and other emulsions and solutions existed, it would eventually be reached if the age of the surface was sufficient. Further, it was conceived that the value of the surface tension would more quickly cease to be a function of time if the emulsion layers contiguous to the surface could be constantly renewed,

because as concentration in the surface takes place concentration of the substance in the emulsion layers just below the surface becomes less. The procedure used to renew the emulsion layers just below the surface skin and to keep the concentration uniform throughout the volume was to circulate gently by sucking it into a 50-c.c. pipette and allowing the content to discharge underneath the surface of the emulsion, disturbing the surface as little as possible. To test this premise, the emulsion was again brought back, by skimming, to a surface-tension value of 72 dynes.\* It was then circulated once, as just described, at intervals of 1 min. and surface-tension measurements were made between circulations; curve *B*, Fig. 5, was then obtained.

That the surface tension of an emulsion becomes constant more quickly by keeping all but the surface in constant gentle circulation is

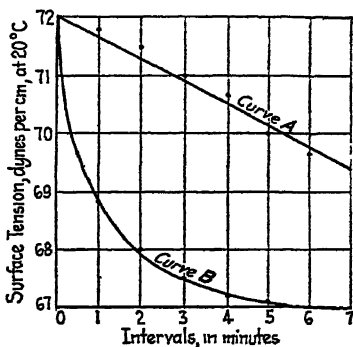


FIG. 5.—EFFECT OF TIME ON SURFACE TENSION OF OIL-WATER EMULSION.

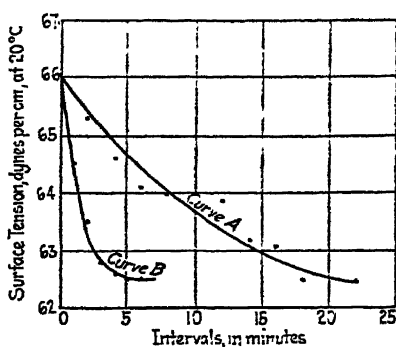


FIG. 6.—INFLUENCE OF CIRCULATION ON RATE OF DROP IN SURFACE TENSION OF AN EMULSION.

borne out by this experiment. To test this point further, an emulsion of one drop of a hardwood creosote oil in 100 c.c. of water was similarly treated; the results of the experiment are plotted in Fig. 6. In this case, after 24 min. standing, the surface tension became constant at 62.6 dynes; the skimmed surface measured 66.2 dynes. The same emulsion skimmed to 66.2 dynes dropped to the same constant, *viz.*, 62.6 dynes, after four circulations, or in 4 min., see curve *B*.

These experiments indicate a true equilibrium point, between the film and the interior, but if this point could be further established by approaching it from two directions it would be more certain. This necessitated starting circulations and surface-tension readings at tensions both above and below the supposed constant or equilibrium point. The low point was obtained by bubbling into the emulsion with a finely drawn tube attached to a hand pump, as used on atomizers. By this process, due to concentration of the oily contaminant on the bubble surface, an excess of the surface-tension lowering constituent was brought

\* Meaning dynes per linear centimeter.

to the free surface resulting in an oversaturated surface and a surface tension below the point of equilibrium.

To test if the surface tensions of two identical emulsions (one skimmed, having a high surface tension, and one bubbled, having a low surface tension) would under the same conditions of temperature arrive at the same value, an emulsion of eucalyptus oil, 12.2 mg. per 100 c.c. water, was made up and so tested. The surface tension of the skimmed surface was 69.0 dynes and that of the bubbled surface 62.1 dynes; the surface tension at the point of adjustment was 63.5 dynes in each case. The data are plotted in curves *C* and *D*, Fig. 7. Curves *A* and *B* are for an emulsion of 5.2 mg. hardwood creosote oil in 100 c.c. water.

From the foregoing experiments, it is obvious that there can be but two possible methods of measuring the surface tension of an emulsion that can be considered reliable. One is a method measuring the tension in a fresh surface, when it would be necessary to define what is meant by a fresh surface and the method would have to measure surfaces of identical age. The other method would be measuring the tension of a surface in which the contaminant is in equilibrium with that in the interior of the emulsion. The film method in combination with circulation measures the equilibrium value and is the method used in nearly all measurements recorded in this paper. One advantage in the use of this method is that small changes in concentration reflect very much greater differences in the surface-tension value than do methods measuring the tension in fresh surfaces. This is of considerable importance in the study of adsorption of surface-tension-lowering contaminants by minerals.

This point is brought out in Fig. 8 which shows surface-tension concentration curves of a steam-distilled pine oil. Curve *A* was obtained from measurements by the Jaeger capillary-bubble method; curve *B*, by the drop-weight method; and curve *C*, by the film method. For example, for 20 mg. of the substance in 100 c.c. of water, by the Jaeger method, the surface tension is 65.8 dynes; by the drop-weight method, 64.4; and by the film method, 59.5. In other words,  $dy/dc$  is, by the three methods, 3.57, 4.3, and 6.72, respectively. If the amount of oil removed from the emulsion is 2 mg., the increase in surface tension indicated by the three methods is 0.7, 0.81, and 1.3 dynes, respectively. With many substances, the difference in range is much greater than shown above. The removal of much smaller quantities of oil by adsorption can be detected by the film method.

The foregoing experiments seem, also, to show that emulsions of flotation oils in water (and it has been found to be true for all pure organic substances worked with, including such soluble substances as the alcohols and butyric acid) have true static surface-tension values; *i.e.*, there is a condition of true equilibrium between surface and interior concentration. For low concentrations, there is an equilibrium point for each

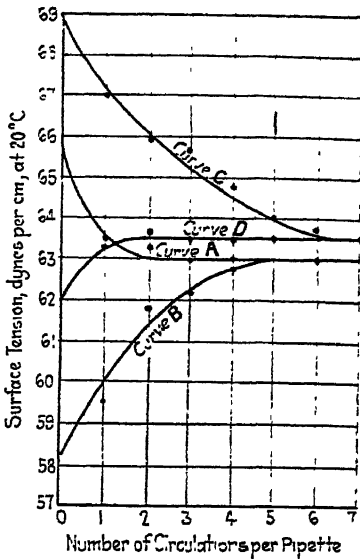


FIG. 7

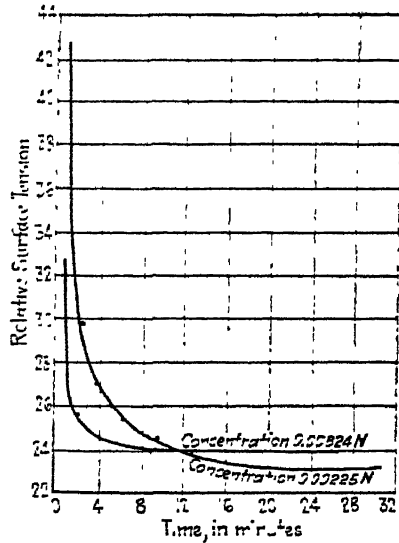


FIG. 9

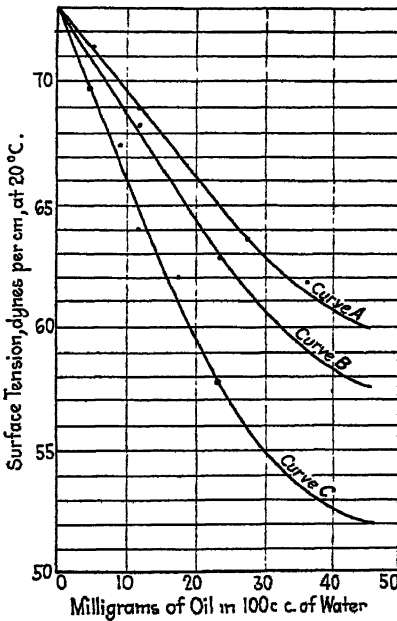


FIG. 8

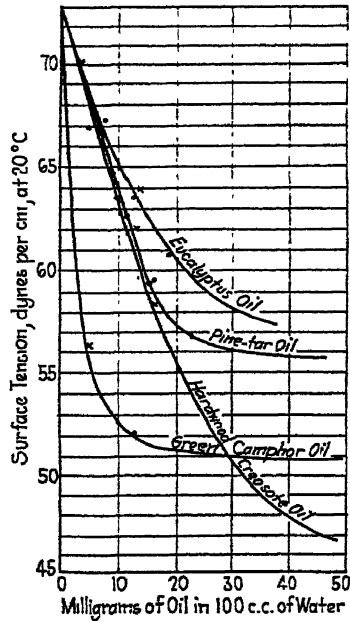


FIG. 10

FIG. 7.—POINTS OF CONSTANT SURFACE TENSION FOR TWO FLOTATION OIL-WATER EMULSIONS.

FIG. 8.—SURFACE TENSION OF A PINE OIL-WATER EMULSION BY THREE METHODS OF MEASURING SURFACE TENSION.

FIG. 9.—SURFACE TENSION OF SODIUM-OLEATE SOLUTIONS AND THE TIME FACTOR.

FIG. 10.—SURFACE-TENSION CONCENTRATION CURVES FOR SEVERAL FLOTATION OILS.



concentration that is a function of the concentration, temperature being constant. When the concentration reaches a certain value, the surface tension ceases to be a function of concentration, and beyond this point, which is not very sharply defined, we have a truly saturated surface film.

Taggart and Gaudin<sup>14</sup> were apparently able to obtain satisfactory reproducible surface-tension measurements on solutions of such substances as phenol and cresol and the soluble portion of pine oils in water by the practice of cleaning their surface-tension plate with acetone and then with ether. All methods of cleaning the plate tried by us failed to remove the disturbing "time factor." It would appear that Taggart and Gaudin measured neither the dynamic nor the static tension but some intermediate tension that experience has shown us is hard to duplicate. On p. 494 (vol. 68), they discuss dynamic tension and static tension in connection with the theory of stable films and foams, but they do not correct their tension measurements so that these will refer either to absolutely fresh surfaces or to mature surfaces. The only time effect mentioned by them is, on pages 505 and 508, in connection with the slow solution of a film of oleic acid in the water beneath it and the accompanying changes in surface tension and, of course, this has nothing to do with the surface tension of emulsions.

Milner<sup>15</sup> showed that the surface tension of an aqueous solution of sodium oleate comes to equilibrium only after several minutes of standing. The curves in Fig. 9 are reproduced from his paper; there surface tension is plotted against time, in minutes.

By the method of circulating emulsions to a constant equilibrium point and measurement of the surface tension by the film method, the surface tension-concentration curves for a number of flotation oils, shown in Fig. 10, were obtained. For convenience in comparing the concentration on these curves with quantities used in flotation practice, it may be stated that 10 mg. of the substance in 100 c.c. of water is equivalent to 0.6 lb. per ton of ore in a pulp dilution of three of water to one of ore.

#### CONSTITUTION OF SUBSTANCES LOWERING THE SURFACE TENSION OF WATER

Almost all organic substances, both of the paraffin series (such as the alcohols, aldehydes, the saturated and unsaturated acids) and of the aromatic compounds and derivatives, lower the surface tension of water. Many of the aromatic hydrocarbon derivatives, however, and such pure hydrocarbons as benzene,  $C_6H_6$ , toluene,  $C_7H_8$ , and cymene,  $C_{10}H_{14}$ , lower it only very slightly; that is, these substances do not spread appreciably on water. The paraffin oils do not spread at all, the halogen derivatives chlorobenzene and bromobenzene, as well as nitrobenzene, spread

<sup>14</sup> *Loc. cit.*

<sup>15</sup> *Phil. Mag.* (1907) 13, 96.

very slowly on water and lower its surface tension but little. A substance that does not lower the surface tension of water will not be adsorbed in its surface; it will, however, go there mechanically and collect in lenticular globules. On the other hand, it may displace water at a solid (such as a sulfide) water surface, but in all the cases tested it does not. Benzene will not displace water at a silver, copper, or glass surface. Such substances are also only slightly soluble in water; they will not cause water to froth. Such a non-spreading substance may be of importance in a certain type of flotation, provided it will displace water at the surface of certain mineral particles. If a particle becomes coated with such a substance, there will be a tendency for particles in a pulp so coated to collect into rather large balls or to aggregate due to the tendency of the water (which has a high surface tension) films to contract to form surface films, in contact with the oiled substances, of minimum area, see Fig. 11.

If, as Taggart and Gaudin have pointed out, oils are adsorbed on mineral surfaces with the polar ends drawn against the mineral surface and with the non-polar ends directed toward the water, mineral particles so coated would behave as if they were coated with a substance such as benzene. A mineral particle so coated would, if brought near the surface,

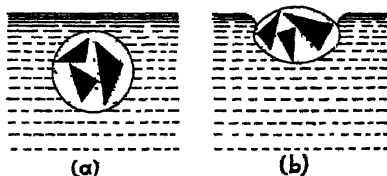


FIG. 11(a).—MINERAL PARTICLES COATED WITH A NON-POLAR OIL. (b) AIR DISPLACING WATER AT OIL SURFACE.

be buoyed up and held on the surface through the contraction of the water film in contact with the oiled particle. This theory was worked out independently by the author and presented at a seminar of the School of Mines, University of Idaho, faculty nearly a year previous to Taggart and Gaudin's publication. The experiments cited by Taggart and Gaudin are fairly convincing but this point seems of such importance that it should be shown more conclusively.

It has been said that substances composed of molecules having "soluble ends," or polar groups, spread on water; and that substances composed of molecules having no soluble portions do not spread. Substances composed of the non-polar hydrocarbon groups and a polar group such as the hydroxyl,  $\text{OH}$ , and the aldehyde,  $\text{CHO}$ , or the carboxyl,  $\text{COOH}$ , group, spread rapidly or slowly, depending on the number of  $\text{CH}_2$  groups in the hydrocarbon chain of the molecule. For example, oxalic acid  $2(\text{COOH})$  is readily soluble in water, so is formic acid,  $\text{HCOOH}$ , and acetic acid  $\text{CH}_3\text{COOH}$ . Propionic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ , is less

TABLE 5

Substance	Concentration	Surface Tension	
		Film Method	Drop-weight Method
H <sub>2</sub> O.....		73.0	73.0
NaCl (c.p.).....	M/1	74.3	75.1
KCl (c.p.).....	M/1	74.3	74.6
KOH (c.p.).....	M/1	73.4	74.2
NaOH (c.p.).....	M/1	73.5	74.8
CuSO <sub>4</sub> (c.p.).....	M/0.5	72.9	73.7

The surface measured by the film method was formed by allowing the solution to run rapidly from funnel *B* into funnel *A*, Fig. 3, which was measured at once. With the drop-weight method, six drops fell every minute. In each case, fourteen drops were weighed in a pan on the same automatic balance that was used for the film method. The measurement is so quickly made that evaporation is negligible. Duplicates were made and what evaporation did take place was considered the same in each case. The surface tension of water was arbitrarily taken as 73 dynes for each method; *i.e.*, a sample of distilled water was measured by each method to obtain the proper factors by which film readings were multiplied and by which the weight of a given number of drops was multiplied.

A saturated NaCl solution, by the film method, had a surface tension of 80.5 dynes at 20° C. Table 6 gives the results obtained for cadmium chloride, CdCl<sub>2</sub>·2H<sub>2</sub>O, and copper-sulfate, CuSO<sub>4</sub>·5H<sub>2</sub>O, solutions.

Baker Chemical Co. c.p. chemicals were used.

TABLE 6.—*Surface Tensions of Salt Solutions*

Chemical	Concentration, Gm. per 100 c. c. H <sub>2</sub> O	Skimmed Surface Tension
CdCl <sub>2</sub> ·2H <sub>2</sub> O.....	70.0	78.0
CdCl <sub>2</sub> ·2H <sub>2</sub> O.....	35.0	76.0
CdCl <sub>2</sub> ·2H <sub>2</sub> O.....	23.3	75.0
CdCl <sub>2</sub> ·2H <sub>2</sub> O.....	11.6	75.0
CdCl <sub>2</sub> ·2H <sub>2</sub> O.....	5.8	74.0
CuSO <sub>4</sub> ·5H <sub>2</sub> O.....	15.9	70.2

A normal sodium-chloride solution of c.p. salt, the surface of which was formed by allowing the solution to run from funnel *B* into funnel *A* and quickly measuring, had a surface tension of 74.4 dynes at 17° C.

This surface had the same tension after standing for 1 hr. covered with an inverted funnel *D*, Fig. 3.

Compression and expansion experiments were made on another portion of the same solution, using the paraffined trough\* shown in Fig. 4. The data in Table 7 were obtained. The compressed surface was

TABLE 7

Area of Surface, Square Inches	Contracted Surface, Per Cent. of Original	Surface Tension, at 20° C., Dynes per Centimeter
48	100.0	75.0
27	56.0	74.9
24	50.0	74.9
21	43.8	73.0
18	48.5	68.6
15	31.4	60.4
12	25.0	51.2
9	18.8	45.0
6	12.4	43.0

again skimmed and had a tension of 75 dynes; it was again compressed as soon as possible after skimming. The tension started dropping when the area was reduced to 8.4 per cent. of the original. A skimmed surface standing 2 min. and one standing 6 min. and then contracted started dropping in tension at surfaces reduced to 18.8 and 37.5 per cent., respectively, of the original area. Skimmings from the surface of the salt solution had a pH value of 8 while the original had a pH value of 4.9, *i.e.*, the surface layer is alkaline while the interior is acid.

The surface of an N/1 solution of KCl enclosed in a ring  $4\frac{1}{2}$  in. in diameter compressed into a ring  $1\frac{1}{2}$  in. in diameter dropped from 74.3 to 46.0 dynes. The compression was effected in funnel *A*, paraffined and graduated so that percentage compression could be read off. On agitating the small portion remaining in the funnel after compression, the tension went up to 63.5 dynes. Whatever may be the nature of the contaminant in these surfaces, it is evident that surface-tension measurements on salt solutions should be made on expanding surfaces.

The tension in a fresh surface of water-containing bases, such as KOH and NaOH in solution, is greater than that of water, but these two, while they do not drop noticeably in short intervals of time, are quite sensitive to compression. A M/1 solution of NaOH had a surface tension of 73.6 dynes per centimeter at 20° C. Acids may lower or raise the surface

\* Experiments were carried out to show that the paraffin had no effect on the surface tension of the solution. Several pieces of paraffin were dropped on to the surface of a salt solution in an Erlenmeyer flask; the surface tension remained unchanged for hours.

tension of water and it has been found that the surface tension of a hydrochloric-acid solution is less affected by time than aqueous solutions of salts or bases. The following tensions were obtained from solutions made with c.p. hydrochloric acid having a specific gravity of 1.18.

QUANTITY HCl PER 100 C.C. H <sub>2</sub> O, CCDC CENTIMETERS	SURFACE TENSION, AT 20° C.
10	72.8
20	72.0
30	71.8
40	71.6
50	71.6

According to Morgan,<sup>18</sup> sulfuric acid up to 5 and 10 per cent. has little effect on the surface tension of water. The maximum increase occurs at about 40 per cent. sulfuric acid. From this concentration up, the surface tension drops off rapidly. We have found that the effect of sulfuric acid in amounts common in flotation practice is to lower the tension slightly.

#### FOAMING OF SALT SOLUTIONS

It is well known that salt solutions foam on shaking. If foaming occurs, something is being adsorbed in the surface films. The substance positively adsorbed (as salt solutions have a higher surface tension than pure water) is presumably the solvent (water). We would therefore expect to find less salt in the foam liquid than in the solution. Surface-tension measurements on the solution and on the foam liquid show that this is the case.

It has been stated that the surface skimmings from various salt solutions are more alkaline than the original solutions. The foams from a sodium-chloride and from a barium-chloride solution were collected and tested for hydrogen ion concentration, with the results shown in Table 8.

TABLE 8.—*pH Value of Foam from Salt Solutions*

Salt	Concentration	pH Value	
		Set 1	Set 2
NaCl, c.p.			
Original NaCl solution.....	N/1	4.9	4.9
Froth.....		5.1	5.0
Residual.....		4.9	4.9
BaCl <sub>2</sub> , c.p.			
Original BaCl <sub>2</sub> solution.....	N/1	6.2	6.3
Froth.....		6.5	6.7
Residual.....		6.2	6.3

<sup>18</sup> *Jnl. Am. Chem. Soc.* (1916) 38, 563.

NOTE.—The distilled water used in making up the barium-chloride solution had a higher pH value than that used in making up the sodium-chloride solution; this accounts for the difference in the pH of the original solutions. It may be argued that a difference of 0.1 pH is insignificant; by direct comparison of solutions, a difference of 0.1 pH gave an unmistakable difference in color. Skimmings from the sodium-chloride solution had a pH value of 8.

The foam liquid was obtained by agitating the salt solution in an Erlenmeyer flask with a soda-fountain drink mixer. Air was supplied through a glass tube leading into the flask. An aspirator pump was used for forcing in the air. The overflowing froth was caught in a cleaned porcelain vessel in which the Erlenmeyer flask sat.

The reason for the interest in knowing what was being adsorbed in the foam film is that ore flotation can be quite successfully done in a laboratory way, in salt solutions. The selective flotation of sulfide minerals from quartz or other gangue minerals in pure salt solutions is of considerable interest from a theoretical point of view. It would be of much interest to know the nature of the adsorption reactions in this kind of flotation.

Sodium chloride and barium chloride are not exactly neutral salts; aqueous solutions of sodium chloride give slightly acid solutions. From experiments made on salt solutions made up of freshly boiled distilled water, it appears that the difference in acidity of the surface solution and the interior salt solution, as shown by skimming experiments, is due to dissolved  $\text{CO}_2$  from the atmosphere. As in the case of boiled distilled water, skimmings from salt solutions made up from freshly boiled water, to remove dissolved gases, showed no difference in acidity for surface and interior solution by the use of indicators. However, if the solutions were allowed to stand in pyrex flasks for several hours and then subjected to skimming tests, noticeable differences in acidity of surface skimmings and residual solution were found.

In all tests for acidity and alkalinity of solutions, a given number of tenths of a cubic centimeter were added to equal quantities of the solution to be tested. The indicators recommended by Clark and Lubs were used. It is interesting that the residual solutions from all skimming tests gave the same color with the indicator as did the original. This subject was insufficiently investigated because of more pressing problems.

#### EFFECT OF CHEMICALS ON SURFACE TENSION OF OIL-WATER EMULSIONS

The only observed effect of chemicals on emulsions when used in the small quantities demanded by commercial practice was, in general, to lower their surface tensions as shown in Table 9. Copper sulfate and sodium dibasic phosphate increased the surface tension slightly.

TABLE 9

Chemical	Pine Oil, Milligrams per 100 c c. H <sub>2</sub> O	Surface Tension at 20° C., Dynes per Centimeter
H <sub>2</sub> O.. . . . .		73.0
H <sub>2</sub> O + . . . . .	18.4	58.7
CuSO <sub>4</sub> , 0.067 per cent. solution + . . . . .	18.4	62.0
Na <sub>2</sub> HPO <sub>4</sub> , 0.067 per cent. solution + . . . . .	18.4	59.3
Na <sub>2</sub> CO <sub>3</sub> , 0.067 per cent. solution + . . . . .	18.4	56.3
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , 0.067 per cent. solution + . . . . .	18.4	57.5
H <sub>2</sub> SO <sub>4</sub> , 0.067 per cent. solution + . . . . .	18.4	56.5
Na <sub>2</sub> S, 0.067 per cent. solution + . . . . .	18.4	56.5
NaOH, 0.067 per cent. solution + . . . . .	18.4	55.6

#### EFFECT OF TEMPERATURE ON THE SURFACE TENSION OF WATER

The temperature of a flotation pulp, in practice, will vary through the year as much as 25° C. As the surface tension of water decreases as the temperature increases, the increment being 0.145 dyne per degree C., there may be a difference of 3 or 4 dynes in surface tension between winter and summer. In some cases, this could easily be a great enough change to cause a noticeable difference in operation results. The change is not only sufficient to cause a lowering of the spreading force of an oil on water, but it may be of considerable importance relative to the question of flocculation and peptization of the mineral particles in water, as was noticed in some work on flocculation of mineral suspensions. The role of flocculation and peptization (or deflocculation) in flotation will be taken up at length in a paper dealing with the solid-liquid interface.

#### ADSORPTION AND WETTING

For convenience of discussion, we may classify adsorption processes into three types, as follows:

*Adsorption type 1*, resulting in a relatively great concentration of the contaminant on the surface of the adsorbent. Examples, adsorption of gases on liquid and on solid surfaces; adsorption of a contaminant on the surfaces of dilute aqueous solution.

*Adsorption type 2*, resulting in the spreading of the contaminant molecules and an orientation of them on the surface. Examples, spreading of relatively insoluble polar liquids (oil, etc.) on water; wetting of solids by liquids.

*Adsorption type 3*, surface concentration followed by solution of the contaminant molecules in the adsorbent. Examples, adsorption of gases by solids, such as hydrogen by palladium; the adsorption of such liquids as acetic acid on water and of mercury by gold.

All three types are important in the flotation process, and the chemical mechanism<sup>19</sup> involved in the three types is the same. The difference manifested is in degree only and, in other respects, due to the physical nature of the components entering into the reaction and in the specific properties of the components. There is no sharp dividing line between these three types of adsorption; they are thus classified simply for convenience.

According to Freundlich, adsorption is always accompanied by a lowering of the surface tension or energy of the adsorbing phase. Willard Gibbs early worked out the mathematical expression for this statement:

$$q = \frac{-c}{RT} \times \frac{dy}{dc}$$

where  $q$  = excess of substance in surface layer;

$c$  = molar concentration of solution;

$R$  = ordinary gas constant, approximately  $83.2 \times 106$  ergs.

$T$  = 293, at 20° C.;

$y$  = surface tension of solution;

$\frac{dy}{dc}$  is determined from a surface-tension concentration curve when  $c$  is known.

This equation is useful in working with substances soluble in water and in concentrations low enough not to give saturated films. When the concentration of the solute reaches a point where the surface tension becomes independent of concentration, the equation is no longer of any use.

The molar concentration in the surface in excess of that in the volume of substances of type 1 can be determined by the Gibbs equation when the solution concentration is somewhat below that which will give a saturated film. Also some cases in class 3 are open to investigation by this formula.

#### SPREADING OF OILS AND OTHER SUBSTANCES ON WATER

This is adsorption type 2. The conditions for the spreading of one liquid on another, for example water, are: The liquids must be immiscible or only slightly miscible in each other; there must be a reaction between the water molecules and certain portions of the molecules of the spreading substance.

It is not necessary that the molecules of each liquid as a whole have mutual attraction for one another. In fact, if this were the case, we would have adsorption of the third type or a solution of one liquid in the other; it is only necessary that the molecules of the liquid contain polar groups.

<sup>19</sup> Langmuir considers that adsorption and surface tension are chemical phenomena [*Met. & Chem. Eng.* (1916) 15, 468] and that the electromagnetic field of force (chemical affinity) surrounding surface atoms is responsible for adsorption.



For example, if a drop of oleic acid,  $C_{17}H_{33}COOH$ , be placed on the surface of clean water, it will immediately spread out over the water surface into a film, which Langmuir<sup>20</sup> has calculated to be one molecule ( $11.2 \times 10^{-8}$  cm.) thick; this is provided the water surface is great enough to accommodate all the molecules. The polar portion in an oleic-acid molecule is the  $COOH$  or carboxyl group. It is soluble in water, meaning that it has a strong affinity for water molecules. The hydrocarbon chain has less affinity for water than the  $COOH$  group and more affinity for oleic-acid molecules; hence it must be pointed away from the surface of the water and the  $COOH$  groups must be pulled down against and, to

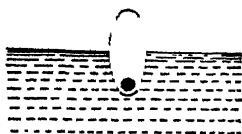


FIG. 12.—ORIENTATION OF POLAR MOLECULAR ON A WATER SURFACE.

some extent, penetrating into the surface of the water. The molecules of oleic acid are considered to stand on end in the water surface much as a light capsule, containing a shot, Fig. 12, would do if thrown on to the surface of water. From Langmuir's and Harkin's work, the general rule has been given that at any surface of contact between two different phases, the molecules in the contact surface, if free to move, will orient themselves so that each end of the molecule points toward or sticks into the phase whose molecules it resembles; in other words, the molecules in the plane of contact will arrange themselves so as to make the transition from one phase to the other the least abrupt. If then a small quantity of oil is placed on a surface of water, it will spread out over the surface until each molecule has its polar group sticking into the water, when spreading will cease.

Substances containing no polar groups will not spread on water. All wood and coal-tar oils of commercial value in flotation contain a preponderance of molecules that contain one or more polar groups. The structure of such oil molecules is no doubt very complex.

The solubility of an organic substance decreases as the length of the  $CH_2$  chain increases. This was pointed out by Traube<sup>21</sup> in 1891. For example, in the formic-acid series, the first members of the series (formic acid, acetic acid, and propionic acid) are readily soluble in water and when a drop of propionic acid is put on water it spreads with a flash but soon disappears, going into solution; this is adsorption of the third type. Caprylic acid,  $CH_3(CH_2)_6COOH$ , of the same series is less soluble, due to the preponderance of insoluble hydrocarbon groups over the soluble  $COOH$  groups, and spreads forming a perceptible film.

That films of oil on water are, in general, one molecule deep has been established beyond doubt. Langmuir's work on oil films on water, which

<sup>20</sup> *Loc. cit.*

<sup>21</sup> *Ann.* (1891) 265, 27.

has been more recently confirmed by others,<sup>22</sup> marks a great advance in our knowledge of the subject.

A flotation oil, such as pine or hardwood oil, spreads rapidly on the surface of clean water, reducing the surface tension to between 40 and 60 dynes per cm., depending on the molecular composition of the oil. If the water is contaminated with any substance, say a water-soluble soap, that lowers the surface tension, the oil will not spread but will collect into lenticular-shaped globules. Substances that hinder or prevent oil from spreading on water would appear to be harmful in flotation.

#### EFFECT OF CHEMICALS ON OIL FILMS ON WATER

Langmuir<sup>23</sup> has shown that films of various fatty acids, alcohols, and esters are extraordinarily sensitive to very small quantities of acid. About one part of HCl in a million of water was sufficient to change his contraction curves for films of stearic acid on water until they hardly resembled the curve for stearic acid on clean water. Sulfuric acid gave exactly the same effect as hydrochloric acid. Regarding salts in solution, such as the chlorides of sodium, calcium, or magnesium, Langmuir states that the contraction curves obtained were not greatly different from those found with distilled water, and that the small effects that do occur with these and other salts are being made the subject of further study.

The effect of acids and bases on oil films on water has been considered recently by N. K. Adam,<sup>24</sup> there is a good deal of speculation about the whole question. The films are soluble to different extents in acid and alkaline solutions. Adam has shown that palmitic acid is completely insoluble in water slightly on the acid side of neutrality, the films preserving their area and properties unchanged for hours. As the alkalinity increases, the molecules are drawn deeper into the water and at a pH value of 10, contraction measurements were impossible because of solution of the films.

#### VARIABLE SURFACE TENSION

In order that a bubble may persist, it must have in the film a substance that is readily adsorbed in the film surface. Thus, if due to

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<sup>22</sup> N. K. Adam: The Properties and Molecular Structure of Thin Films of Palmitic Acid on Water. *Proc. Royal Soc. (London)* (1921) 99A, 336.

Paul Woog: The Dimension of the Molecules of the Fatty Oils, and Certain Phenomena of Molecular Solution. *Comptes Rendus* (1921) 173, 387.

A. Marcelin: Surface Tension of Monomolecular Layers. *Comptes Rendus* (1921) 173, 38.

<sup>23</sup> *Jnl. Am. Chem. Soc.* (1917) 39, 1875.

<sup>24</sup> *Loc. cit.*

sudden local outside forces, the film is caused to stretch at certain points, resulting in a raising of the surface tension; at that point, some of the substance will be quickly adsorbed in this portion of the surface film and a uniformity of tension is quickly established.

This equalization of forces by the adsorption of a surface tension-lowering constituent is active in foaming and in the formation of mineral froths. The presence of the large number of fine mineral particles in the spongelike structure gives added stability to the froth as a result of decreased mobility.

### SURFACE TENSION OF BUBBLES IN A FLOTATION PULP

The surface tension, or the tension existing at an aqueous pulp-air (bubble) interface, cannot be determined experimentally but there is every reason to believe that in flotation practice it is very little less than that of clean water. This statement applies to the water-bubble surface before the bubble reaches the free surface of its pulp. In modern flotation practice, the amount of oil used, when thoroughly mixed into the pulp, lowers the surface tension of the pulp only very slightly, in the neighborhood of 60 to 70 dynes per cm. After treatment, the tailing pulp will have a surface tension usually around 71.5 dynes per cm. These figures will vary with the kind and quantity of oil used, but it is never much below that of pure water. The tension of skimmed surfaces, as measured by the film method, corresponds more nearly to the tensions existing in a flotation pulp than do the values of surface tension obtained on circulation of the emulsions, or what may be called the static surface tension. The latter will be much lower than the tension of a fresh surface, such as that existing at the pulp-bubble interface. In some respects, therefore, the dynamic tensions are of greater interest. With a pulp of low surface tension and a high surface concentration of contaminant, the selective adsorption of minerals for oils disappears and the condition of over-oiling, familiar to the millman, appears.

If the surface tension of the pulp is as high as the figures given, it is reasonable to suppose, in view of the large number of bubbles in a properly aerated pulp, that the bubble-water surface tension is practically that of water. Thus there is a strong tendency for the oil to go into the bubble surface; *i.e.*, the rate of adsorption is a maximum. The greater the number of bubbles, the higher will be the surface tension and the cleaner should be the concentration. The desirability of high surface tension will be made evident when we examine an oil-water emulsion. If the surface of an oil-water emulsion is skimmed with a strip of paraffined paper and its surface tension measured, it will be found, for a short time, to have a high surface tension, see Fig. 6; there will be a rapid rate of surface concentration at this point. As the tension drops, the rate will

decrease; and at the point of equilibrium in surface concentration, there will be no effective surface concentration.

### SUMMARY AND CONCLUSIONS

1. The modern theories of the structure of matter in their relation to the theory of flotation are touched on. Polar and non-polar substances are defined. Flotation oils fall into the class of polar substances and possess, from a flotation standpoint, the important properties of spreading on water, of lowering the surface tension of water, and of adsorbing on mineral surfaces.

2. The latest design of the writer's apparatus for measuring surface tension by forming films is shown and described. With this method, the tension of liquid surfaces of any age greater than a few seconds is conveniently measured and the surface tension of a liquid can be determined to an accuracy of  $\frac{1}{2}$  per cent. in a couple of minutes.

3. Methods for compressing liquid surfaces are described.

4. The surface tension of water, as affected by various gases and in vacuo, is discussed and a table of data compiled from the work of various observers is given, from which the following facts are apparent: There is no agreement among the various observers as to the effect of various gases on the surface tension of water or as to the value of the surface tension in vacuo. There is little change in the surface tension of water in contact with various gases other than carbon monoxide, which seems to lower it slightly. The conclusion is that the lack of concordancy is to be attributed to experimental error or to surface contamination or to both.

5. Data are given to show that the surface tension of water, as determined by the film method, remains constant with age, up to 48 hr., if the proper experimental precautions are taken. It has been found next to impossible to maintain absolutely uncontaminated surfaces for any length of time.

6. Surface compression experiments on water are given that show: That the surface tension of aged surfaces drops off rapidly when squeezed between two paraffin blocks; that the point in the compression where the surface tension falls off bears a relation to the age of the surface. The explanation for this is probably in the presence of contaminants adsorbed on the surface, the source of such contaminant being from the air, dissolved substances in the water, or oils from the paraffin.

7. Flotation oil-water emulsions, in low concentrations, have constant surface-tension values, which are reached only after several hours of standing but which are more quickly reached by keeping the emulsion in gentle constant circulation. Different methods of measuring surface tension give widely varying results for the surface tension of flotation oil-water emulsions; the magnitude of the value is in relation to the age of the surface. The fresher the surface the higher is its surface tension.

8. Substances possessing no polar or active groups in the molecules, such as benzene and paraffin oil, are of no value as pure substances in modern flotation methods. Only substances that possess the property to spread on water have been successfully used in flotation.

9. The surface tensions of water on which various flotation oils have spread are given. The spreading coefficients of a number of substances are determined.

10. The effects of chemicals on the surface tension of water are investigated. A tabulation of the figures of a number of observers for the variation of the surface tension of water with concentration of potassium chloride shows a total absence of agreement.

11. The surface tension of aqueous solutions of salts and bases drops with age of the surface and rapidly on compression. The older the surfaces, the earlier in the compression does the drop of tension commence.

12. For salt solutions, hydrogen-ion concentration determinations by the use of indicators indicate that the falling off in tension with age and with compression is caused by a surface concentration of alkalinity. This probably explains the lack of agreement in the values of the surface tension of potassium-chloride solution in the table as recorded by various observers.

13. Hydrogen-ion determinations on foam liquid from several aqueous salt solutions indicate the foam to be more alkaline than the interior solution. Carbon dioxide dissolved in the solution seems to be the factor responsible for this surface condition.

14. Adsorption and wetting in their relation to flotation are discussed.

#### SURFACE REACTIONS WITH SPECIAL REFERENCE TO THE LIQUID-LIQUID INTERFACE

In the present froth-flotation process, such small quantities of oils are used that there is some speculation as to what happens at the interface of the oil droplets in contact with the water. In the past, considerable stress has been placed on the question of emulsification although without sufficient evidence that an emulsion of oil-in-water or of water-in-oil really existed. Megraw<sup>25</sup> thinks that, in flotation, we are specifically not dealing with an emulsion of oil-in-water and that if we were we could not get flotation. Moses,<sup>26</sup> using Bancroft's ideas of emulsions, accounts for them in flotation by the presence of adsorbed films and thinks that sulfuric acid is usually beneficial due to its ability to drive away these adsorbed films and thus destroy the emulsion. Van Arsdale has taken out patents covering the use of sulfuric acid to break up

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<sup>25</sup> "The Flotation Process," 30. 1916.

<sup>26</sup> Agitation in Flotation. *Eng & Min. Jnl.* (1921) 123, 477.

emulsions in flotation. It is evident that there is much uncertainty as to the part played in flotation by that portion of the flotation agent (oil) which is insoluble in water and which must take the form of very tiny droplets in the continuous water phase.

Such questions as the following at once confront us: (1) In present flotation practice are the oily substances completely soluble in the small quantities used? (2) If the oil is not completely soluble, what is the condition of the insoluble portion in the water? (3) What is the part played by the oil in these two conditions? Much light can be thrown on these questions by a study of the nature of the interface of oils in contact with water, with respect to interfacial tension and adsorption. Soluble substances in flotation will not be discussed here, except to say that there are completely soluble substances that cause flotation.

#### CLASSIFICATION OF SUBSTANCES OF POSSIBLE VALUE IN FLOTATION

For the sake of discussion, we may classify the substances of possible value in flotation as follows:

1. Soluble or polar substances: with these substances no interface will be formed as they are soluble in water beyond concentrations of interest in flotation. Examples are phenol, cresol, alpha-naphthalamine and amyl alcohol. These substances have not found wide use as such and are usually mixed with less soluble substances. These will not be discussed.

2. Substances composed of molecules having one or more "soluble" groups, called polar groups, which may be subclassified as follows: (a) Substances in which the soluble polar end predominates and which are soluble far in excess of the quantities used in flotation. Examples are the short-chained alcohols (OH group), aldehydes (CHO group), and some of the fatty acids (COOH group) of the formic-acid series. No interface will be formed. Many of the substances in this class assist flotation. (b) Substances in which the non-polar group, or "insoluble" portion, in the molecule predominates. Examples are many flotation oils and the long-chained fatty acids, such as oleic acid. These substances are only very slightly soluble and at present are the most generally used in the flotation process. When these substances, in the quantities used in flotation, are agitated with water, presumably a part goes into solution and a part becomes emulsified in the water. All substances that spread on water and form a film belong in this class. In small quantities, these substances lower greatly the surface tension of water and are, therefore, good foaming agents.

3. Insoluble slightly polar substances: there are relatively few non-polar substances. Paraffin oils are examples of such substances. They do not spread on water, do not dissolve in it and thus do not lower its surface tension, and will not promote frothing. As the present flotation process requires a substance that lowers the surface tension of water and

which is strongly adsorbed in the surface, substances in this class are of little importance. These substances are not only of no use as "frothers," but they are displaced at the surfaces of most solids by water. They, therefore, are also not "oilers" in those cases.

### INTERFACIAL TENSION

The interfacial tension of two immiscible substances *A* and *B* is defined as the force, in dynes per centimeter, required to pull a film (of negligible thickness) of *A* into substance *B* or of *B* into *A*. Antonov<sup>27</sup> has shown that the interfacial tension between two liquids *A* and *B* is the difference between the surface tension of *A* saturated with *B* and the surface tension of *B* saturated with *A*. That Antonov's rule holds fairly closely has been shown by the more recent work of Reynolds.<sup>28</sup>

### METHODS OF MEASURING INTERFACIAL TENSION

Methods of measuring interfacial tension may be divided into statical and dynamical. Of the statical methods that of Quincke, based on a consideration of the dimensions and shape of the drops of one liquid lying at rest in a surrounding immiscible liquid, the capillary-rise method of Reynolds, and the film method just described are available. Only one method that may be called dynamical has been used at all extensively; *viz.*, that based on considerations of the forces operating on a drop of one liquid forming in a second immiscible liquid, or known as the *drop-weight method*.

The capillary-rise method has been developed to a high degree of accuracy by Reynolds, who gives the following requirements for its use: "An essential condition is that the perfectly cleaned tube must be completely filled with the liquid which has the greater surface tension (in general, an aqueous solution), and the other immiscible liquid must travel continuously in one direction only. The measurements are completely falsified if the aqueous solution is allowed to advance along a surface that has been wetted by an immiscible organic solvent, as even in the simplest cases, such as benzene-water, it takes many hours to displace the former completely and, in many cases, the displacement is not complete after several weeks' contact." Perfect cylindrical capillary tubes are also necessary.

The drop-weight method has been most highly perfected by Harkins<sup>29</sup> and his students, who found the capillary-tube method inaccurate in the measurement of interfacial tension particularly in working with a benzene-water interface. Harkins, Davies and Clark<sup>30</sup> state, "The fact

<sup>27</sup> Interfacial Tension II. *Jnl. Chem. Soc.* (1921) 119, 466.

<sup>28</sup> Russ. Phys. Chem. Soc. 39, 120-121, 93, 342-53.

<sup>29</sup> *Jnl. Am. Chem. Soc.* (1919) 41, 499.

<sup>30</sup> *Jnl. Am. Chem. Soc.* (1917) 39, 549.

that the capillary-tube method in no case gave the same results in duplicate determinations unless the time the solution was kept in the tube was nearly the same, and that even quartz capillaries gave very poor results, suggests that the capillary-height method is not suited for such a problem as this."

From a consideration of the figures of Reynolds, which indicate an exceedingly high degree of accuracy, it appears that certain factors, which will be brought out later, were not recognized or were not given due consideration by Harkins, and his coworkers. Table 10, taken from Reynolds' paper, brings out the differences in the values of interfacial tensions depending on the method used. It is to be noted that the supposedly statical method gives the higher value in all cases. This is contrary to what would be expected but is to be explained by the fact that the capillary-rise method as used by Reynolds is more dynamical than the drop-weight method.

TABLE 10.—*Values of Interfacial Tensions and Methods of Measurement*

Substance	Method	
	Statical (Capillary-rise)	Dynamical (Drop-weight)
Ether and water.....	10.6	7.7
Amyl alcohol and water. . . . .	4.8	3.8
Benzene and water.....	34.0	28.0
Nitrobenzene and water. ....	24.7	21.0
Chloroform and water.....	33.3	26.7
Carbon tetrachloride and water . . . . .	43.8	34.1

The film method, which so far as the writer knows has not been used heretofore for measuring interfacial tension, is a truly statical method. The apparatus is shown in Fig. 1. One design of the frame is shown in Fig. 13. It is used when the layer above the interface is only about 1 mm. deep and when it displaces the lower phase at the surface of the frame, *i.e.*, when the film is formed by lowering the frame through the interface. Another design, which is similar to that used in surface-tension work, is shown in Fig. 14. This one is more satisfactory when the upper phase is about  $\frac{1}{2}$  in. deep and when the film is formed by drawing the frame up through the interface. It eliminates entirely the question of the buoyancy of the frame in the liquids. Its position at the stage of the measurement when the film is formed is shown in (c).

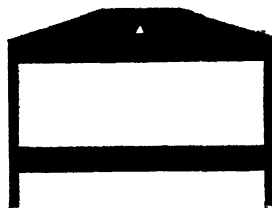


FIG. 13.—PLATE USED FOR INTERFACIAL TENSION MEASUREMENTS.



With the film method, a film of either liquid may be drawn into the other and a film of the substance that most easily wets the frame should be formed. This method has the advantage of being rapid and, as against the drop-weight method, is applicable to the study of surface concentration when this is influenced by time. In other words, slow adsorption processes are readily investigated by this method, while they are not by dynamical methods; and, heretofore, many important phenomena have

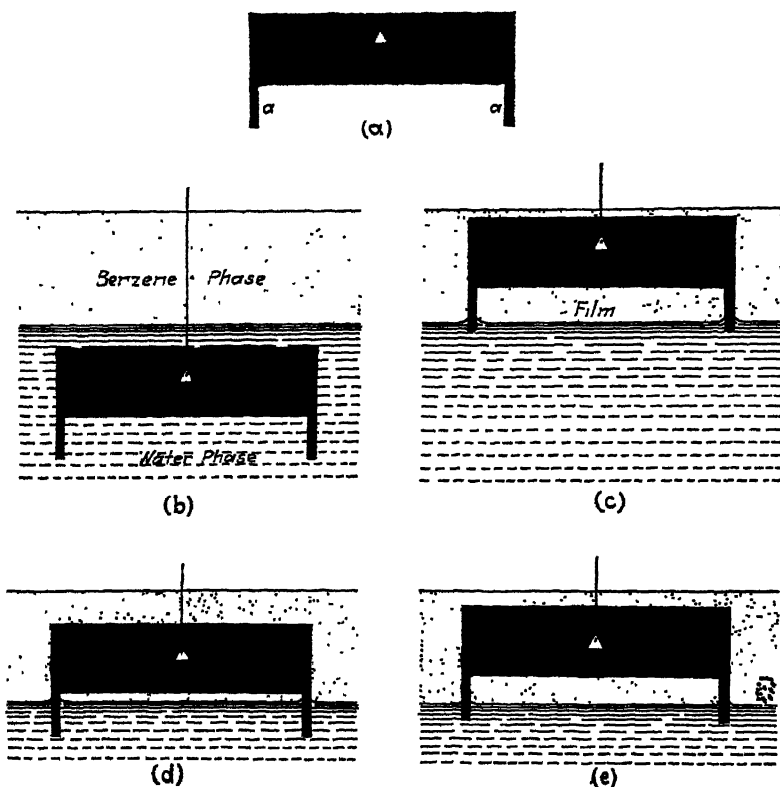


FIG. 14.—(a) ANOTHER FORM OF PLATE USED IN INTERFACIAL TENSION MEASUREMENTS. (b)–(e) STAGES IN THE OPERATION OF MAKING AN INTERFACIAL-TENSION DETERMINATION.

escaped the attention of experimenters through the inability of their methods to detect such changes of adsorption as occur with the age of the surfaces.

The film method has the disadvantage, when the tension in the film is measured on the automatic balance, of being slightly less accurate than either the capillary-rise or the drop-weight. However, readings are easily possible to 0.1 to 0.3 dyne, which is sufficiently close for this work and many other kinds of investigations involving interfacial-tension measurements.

Another source of discrepancy in this method, when applied to interfacial tension, is to be found in the wetting of the vertical portions *a* of the frame, Fig. 14, to which the ends of the ribbon-shaped liquid film are attached. With some oils, unless great care is exercised, the contact angle of the respective liquids against the uprights *a* of the frame will be different when the film is attached and when it is broken; as the tension in the film is taken to be the difference between that recorded when the film is formed, and after it is broken and the frame occupies the same position, relative to the interface, the contact angle should be the same in both cases. The error from this source is kept at a minimum if the upright members of the frame are made as narrow as possible and if the procedure here outlined is followed. For example, if the benzene water interfacial tension is to be measured, the water should be put into the beaker, the beaker raised by means of the adjustable stand until the frame hangs free and is completely immersed in the water, as in Fig. 14(b), then the benzene layer should be added. The beaker should then be lowered by operating the adjustable stand, slowly pulling the frame up through the interface forming the film, as shown at (c). The position of the pointer on the scale is next recorded and the film ruptured. The frame should now be lowered until the straight edge nearly engages the water phase, as shown at (d), and then raised to the position relative to the interface that it occupied when the film was attached, as in (e). By this procedure, in the case of a benzene-water interface, providing adsorption of a substance in the interface is not taking place, duplicate readings that check to within 0.1 dyne are possible.

#### TENSION AT OIL-WATER INTERFACES

Table 11 gives the results of measurements made on interfaces of several substances in contact with water, each phase being presumably

TABLE 11.—*Interfacial Tension of Some Substances Against Water by Calculation and by Observation*

	Surface Tension of Dry Oil	Surface Tension of Oil Saturated with Water	Surface Tension of Water Saturated with Oil	Interfacial Tension		
				Calculated	Observed	Temperature, Degrees C.
General Naval Stores No. 5, steam-distilled pine oil.....	31.3	31.0	43.0	12.0	11.3	20
P. T. & T. Co., No. 100 pine oil..		30.7	47.0	16.3	13.3	19
Oleic acid.....		36.2	46.2	10.0	12.0	19
P. T. & T. Co. ref. pine oil.....		37.0	50.0	13.0	13.2	19
Green camphor oil.....		36.2	50.5	14.3	14.0	19

saturated\* with the other. As a check, the values of the surface tension of the water saturated with the oil in contact and of the oil saturated with the water are given. Of interest in this connection are the interfacial tensions, Table 12, given by Reynolds (*loc. cit.*) of several common substances in contact with water, as determined by calculation and by observation.

TABLE 12.—*Interfacial Tension by Calculation and by Observation by Reynolds' Capillary-rise Method*

Substance	Surface Tension of Water Saturated with Oil	Surface Tension of Dry Oil	Surface Tension of Oil Saturated with Water	Interfacial Tension		
				Calculated	Observed	Temperature, Degrees C.
Benzene.....	63.2	28.4	28.8	34.4	34.4	19
Ethyl ether.....	28.1	17.7	17.5	10.6	10.6	18
Aniline.....	46.4	41.9	42.4	4.2	4.8	26
Chloroform.....	59.8	27.2	26.4	33.4	33.3	18
Carbon tetrachloride.....	70.2	26.7	26.7	43.5	43.7	17
Nitro benzene.....	67.9	43.4	43.2	24.7	24.7	18

For flotation oils, but better still for pure substances in contact with water, the interfacial tension is approximately determined by the rule of Antonov. The tension at the interface between water and a viscous immiscible substance is probably not accurately measured by the film method to closer than 0.5 dyne, but for benzene and light thin oils, a higher degree of accuracy is attainable. The interfacial tension of a given two-phase system and the extent to which it is altered by contaminants in either phase are important questions in flotation.

#### EFFECT OF CHEMICALS ON INTERFACIAL TENSION

Acids in the quantities used in flotation have practically no effect on the tension of a normal or uncontaminated interface. A difference, beyond the range of experimental error, for a number of flotation oils, and for different concentrations of HCl could not be obtained. Reynolds<sup>31</sup> gives 35 dynes for the interfacial tension of benzene against a  $\frac{1}{2}$ N H<sub>2</sub>SO<sub>4</sub> solution and 36.6 dynes for a  $2\frac{1}{2}$ N solution. It is known, however, that acids are very effective in breaking up emulsions and it is generally agreed that this is through adsorption of the hydrogen ions which neutralize part or all of the negative charge that emulsoid particles are known to carry.

\* Saturation was effected by allowing the phases to stand in contact with each other for 48 hr., a portion of each phase was then transferred to a clean beaker, thus forming a new interface.

<sup>31</sup> *Loc. cit.*

Bases lower the interfacial tension between water and substances in the second and third groups of substances of doubtful value in flotation. For steam-distilled pine oil, General Naval Stores No. 5, the results in Table 13 were obtained by the film method:

TABLE 13.—*Effect of Sodium Hydroxide on the Pine Oil-water Interfacial Tension*

Mg. NaOH in 100 c.c. H <sub>2</sub> O	Interfacial Tension, Dynes per Cm. at 15° C.
	11.2
2.0	8.7
4.0	6.4
6.0	7.3
8.0	6.6
20.0	6.2
40.0	5.2
60.0	4.4
80.0	4.3
100.0	3.3

Harkins, using the drop-weight method of measuring interfacial tension, showed that sodium hydroxide has practically no effect on the tension of the benzene-water interface. He found that there was a drop in interfacial tension of only 1 or 2 per cent. and then, for higher concentrations than 0.001N, the interfacial tension rises with the concentration of the base. He thinks this very small drop is probably caused by the electrocapillary effect. The results of sodium hydroxide on the benzene-water interface given in Table 14 were obtained by the film method.

TABLE 14.—*Effect of Sodium Hydroxide on the Tension of a Benzene-water Interface*

Mg. NaOH in 100 c.c. Water	Interfacial Tension, at 20° C.	Mg. NaOH in 100 c.c. Water	Interfacial Tension, at 20° C.
0 00	34.4	13.8	22.5
2.33	28.4	18.8	22.0
3.47	27.7	22.0	21.4
4.50	26.3	24.8	18.2
5.70	25.8	28.0	18.4
6.70	24.4	37.0	18.3
7.75	23.5	107.0	16.2
9.90	23.2	625.0	15.8
11.6	22.8		

TABLE 15.—*Adsorption of Substances at a Hydrocarbon Oil-water Interface*

Substance	Adsorption of Cation, Gm. per Cm. <sup>2</sup>		Adsorption of Anion, Gm. per Cm. <sup>2</sup>	
	Found Value	Calculated from Gibbs' Equation	Found Value	Calculated from Gibbs' Equation
Silver nitrate.....	$2.5 \times 10^{-8}$	$4.5 \times 10^{-8}$		$2.3 \times 10^{-8}$
Potassium chloride.....	$5.0 \times 10^{-8}$	$1.7 \times 10^{-8}$	$10^{-8}$	$1.6 \times 10^{-8}$
Barium chloride.....		$3.0 \times 10^{-8}$	not greater than $10^{-8}$	$1.6 \times 10^{-8}$
Copper chloride.....	$3.5 \times 10^{-8}$	$2.0 \times 10^{-8}$	$2 \times 10^{-8}$	$2.0 \times 10^{-8}$

As Lewis points out, there is evidence of slight selective adsorption, the cation more than the anion, which he thinks is probably due to electrical effects as the oil is shown to be negatively charged and the potential difference between the oil and water is approximately 0.05 volt. The hydrocarbon oil used by Lewis was highly non-polar, non-spreading, and inert toward water, as is evidenced by its high interfacial tension (45.81 dynes) against water. Also all of the salts lowered the normal interfacial tension. The interfacial-tension concentration curves are given in Lewis' paper. It would seem that, as far as emulsification is concerned, the film method is measuring what we are interested in knowing, for bases certainly assist in the emulsification of benzene in water.

#### EFFECT OF SALTS ON INTERFACIAL TENSION

Salts, such as sodium chloride, in small quantities have practically no effect on oil-water interfacial tensions, but in high concentrations they increase it noticeably, *i.e.*, with reference to fresh surfaces. Reynolds<sup>37</sup> gives for the interfacial tension of benzene against 0.1/M, 1/M, and 5/M solutions of NaCl, 34.9, 37.3 and 42.5, respectively. On the other hand, W. C. M. Lewis<sup>38</sup> gives data for the interfacial tensions of potassium-chloride, barium-chloride, copper-chloride, and silver-nitrate solutions and a hydrocarbon oil that show that these salts lower the interfacial tension. Table 16 is compiled from Lewis' paper.

Inasmuch as the foam and surface skimmings of salt solutions are more alkaline than the bulk of such solutions and the surface tension drops on contraction of aged salt-solution surfaces, we might expect the tension of a salt solution-benzene interface to drop somewhat with age of the surface; this is the case but the decrease is very slight. Such substances as  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{HPO}_4$ , which are frequently used in flotation, lower

<sup>37</sup> *Loc. cit.*<sup>38</sup> *Loc. cit.*

TABLE 16.—*Effect of Salts on Hydrocarbon Oil-water Interfacial Tension, from Lewis*

Substance	Concentration, in Gram-moles per Liter	Tension, Dynes per Centimeter
	Normal water-oil tension	52.0
Silver nitrate.....	0.04	47.3
Potassium chloride. ....	0 10	47.8
Barium chloride, saturated solution 34.00 per cent. anhydrous.....	1.70	15.48
Copper chloride.....	0.10	45.8

the tension only slightly. They do, however, greatly affect the concentration of mineral suspensions in the interface. This was shown by agitating mineral suspension in the water phase with a wire loop. Galena readily collects at the interface of benzene-water containing sodium phosphate, while sphalerite does not.

#### EFFECTS OF COLLOIDS ON INTERFACIAL TENSION

Experiments have shown that such substances as lampblack, colloidal clay, and finely powdered minerals have practically no effect on oil-water interfacial tensions. It is hardly to be expected, as they do not alter the free surface tension of water.

Such substances as water-soluble soaps (sodium and potassium oleates, palmitates, etc.) should be expected to lower the tension at an oil-water interface, because they reduce greatly the surface tension of water. It is found, however, that the very small quantities required to lower the surface tension of the water to a point where the oil would not spread on it have practically no effect on the interfacial tension of the oil on the soap solution. Sodium oleate or potassium palmitate, up to 250 mg. in 100 c.c. of water, has no effect detectable within the range of accuracy of the method used, which is from 0.1 to 0.5 dyne. Ten milligrams of potassium palmitate in 100 c.c. of water reduce the surface tension to 45.5 dynes. On this solution, flotation oils do not spread; the interfacial tension for steam-distilled pine oil and this solution is 11.1 dynes, which is only 0.1 dyne below that of the oil on pure water. This difference is, of course, insignificant.

The interfacial tension of benzene on a 2.5-per cent. sodium-oleate solution was found to be 1.6 dynes per centimeter at 20° C. The surface tension of the benzene saturated with this solution was 29.5 and the surface tension of the solution saturated with benzene was 31.2, at 20° C. As soap has little effect on interfacial tension in quantities that correspond to from 5 to 10 lb. per ton in flotation practice, it is doubtful if any harm

they may do is to be attributed to emulsification. It must be remembered, however, that there is a concentration of these substances at the oil-water interface in even these concentrations but the rate is slow, as will be shown later. Harkins, Davies and Clark<sup>39</sup> give the data in Table 17 for the effect of sodium oleate on a benzene-water interface. That not all colloids lower the interfacial tension at a liquid-liquid interface is made clear by the figures given in Table 18, for a benzene-water interface, taken from Reynolds' work.

TABLE 17.—*Effect of Sodium Oleate on Interfacial Tension of Benzene-water*

Sodium Oleate	Surface Tension, in Dynes at 20° C.
0.0000	35.03
0.003N	20.63
0.005N	9.00
0.007N	5.85
0.014N	2.22
0.03N	2.05
0.0436N	2.09
0.1N	1.78

TABLE 18.—*Effect of Colloids on Interfacial Tension of Benzene and Water*

Solution	Interfacial Tension after	
	15 Minutes	24 Hours
Water.....	34.4	
0.5 per cent. gelatine.....	21.0	19.9
0.1 per cent. gelatine.....	26.1	23.4
10 per cent. acacia.....	32.9	25.9
5 per cent. acacia.....	34.6	29.9
1 per cent. acacia.....	36.3	34.5
0.5 per cent. tragacanth, 0.32*.....	25.9	19.2
2 per cent. arrowroot, 0.488*.....	36.3	35.7
2 per cent. patent starch.....	36.3	36.3

\* Per cent. concentration after clarification.

It is interesting to note that here again the rate of adsorption is rather slow. The 15-min. results were obtained by the drop-weight method, and the 24-hr. results by the capillary-rise method. The

<sup>39</sup> *Jnl. Am. Chem. Soc.* (1917) **39**, 588.

case of patent starch is interesting in that there is no change in tension with time; the explanation is probably in the nature of the sign of the electrical charge on these colloidal particles and on the interface.

All of the colloid substances shown to lower the interfacial tension are detrimental in a flotation pulp. They hinder frothing by oils in that they decrease the spreading coefficient of the oil in the water; also, in that they probably hinder the active groups in the oil droplets from coming in contact with and spreading on mineral particles. Such substances, because of their strong adsorption properties, constantly intervene and prevent contact of mineral and oil and oil and water.

#### CONDITION OF SUBSTANCES OF CLASS 2(b), OR FLOTATION OILS IN WATER

A substance, such as a flotation oil, that spreads on water and, therefore, contains groups in the molecules that are strongly polar, or soluble in the water, can exist when mixed with water in two possible combinations: (1) completely dissolved in the water; (2) partly dissolved with the undissolved portion emulsified in the water.

Substances, such as amaroil and nujol, that do not spread on water and therefore have no polar groups can exist mixed with water in only one of two possible forms: (1) as droplets of the substance in water; or (2) as droplets of the water in the substance, depending on the relative proportions of the two admixed.

Summing up the matter, substances of classes 1 and 2 (a), p. 677, when agitated with water in concentrations considerably above any used in flotation are in true solution, *i.e.*, the soluble portion of the molecule easily predominates over the insoluble portion. Substances of class 2(b) are slightly soluble in water and it is a little difficult to determine exactly how they exist when mixed, in small quantities, in water. Substances in class 3 always form very unstable emulsions in water. It is unfortunate, for the flotation investigator, that it is with substances of this class that most of the work has been done, while little has been done on such systems as would result from mixtures of a polar substance in water, which are of special interest to us.

We will eliminate from our consideration completely soluble substances (class 1), as they form no interface with water, and completely insoluble substances (class 3), as they have not yet found application in flotation practice, and confine ourselves to a study of substances falling in class 2(b), in which most flotation oils belong.

#### SURFACE TENSION-CONCENTRATION CURVES AND THE CONDITION OF OILS IN WATER

From surface tension-concentration curves of a number of flotation oils, Fig. 10, the following facts are evident:



For each substance, up to a certain concentration  $x$ ,\* the surface tension is closely a linear function of the concentration. The  $ds/dc$  values for the substances between zero and  $x$  concentrations are as follows:

SUBSTANCE	$ds/dc$ AT 20° C.
Eucalyptus oil . . . . .	0.75
Pine-tar oil . . . . .	0.90
Green camphor oil . . . . .	5.2
Hardwood creosote oil . . . . .	0.94
Caproic acid . . . . .	4.8

Beyond the points  $x$ , the surface tension decreases less rapidly with concentration and finally becomes independent of concentration and the surface tension-concentration curves run horizontally. Along this part of the line we have saturated surface films.

The emulsions are quite stable for concentrations in the range for which  $ds/dc$  is constant. Little difficulty is met in getting reliable surface-tension measurements by the film method within this range; beyond, where the adsorbed molecules or micellæ begin to pack in the surface film, it is more difficult to get reliable surface-tension measurements, even by circulation. If we wish to investigate concentrations beyond the point  $x$ , some other method must be used.

The fact that the surface tensions of the substances for which curves are plotted in Fig. 10 are, for very low concentrations, linear functions of the concentration, seems to indicate that they are soluble in water or, if not soluble, in a condition that simulates a true solution. If they are not true solutions in these low concentrations, and there are indications in some cases that they are not, as they are turbid to the unaided eye, they are emulsions of oil droplets or aggregates of molecules or micellæ in water, the water being the continuous phase.

Flotation oils have an effect on the surface tension of water entirely similar to soaps, such as sodium or potassium oleate and palmitate. Their effects are, however, less abnormal. According to McBain, soaps in colloidal solution, or in solution as molecular aggregates, are effective in lowering the surface tension in proportion to the size of aggregate or micellæ. Walker,<sup>40</sup> who uses McBain's ideas, makes the following statements:

To bring this theory in line with facts, we must assume that very large micellæ are not so active, weight for weight, in lowering the surface tension of soap solutions as those of moderate size. Therefore, if the size of the colloidal aggregates is increased beyond a certain limit, there is a falling off of efficiency, even though the surface concentrations may remain high, such an assumption is reasonable in view of the fact that the special forces active in the surface layer only penetrate beneath the surface to an extent depending on the range of molecular action. Therefore, when the colloidal

\* See points  $x$ , on curves Fig. 10.

<sup>40</sup> Surface Tensions of Salts of the Fatty Acids and their Mixtures. *Jnl. Chem. Soc., London* (1921) 119, 1521.

particles reach dimensions which are large in comparison with molecular magnitudes, a falling off in efficiency must necessarily be expected.

Walker then classifies micellæ into: (1) small micellæ efficient in lowering the surface tension, but difficult to chain to the surface on account of their relatively high osmotic pressure; and (2) large micellæ inefficient in lowering the surface tension, but easy to chain to the surface on account of their relatively low osmotic pressure. Walker continues with this line of reasoning as follows:

When the soap solution is extremely dilute, the concentration in the surface layer will be sufficiently small for the soap to consist mainly of simple molecules. As the concentration increases, complexes will increase in the surface layer, slowly at first and then with increasing rapidity. The more complexes are formed, the smaller will be the work required to be done by surface tension against the osmotic pressure in order to concentrate the soap in the layer . . . As soon as the point is reached at which an increase in concentration is associated with an actual decrease in osmotic pressure, followed by a region in which the osmotic pressure rises slowly with concentration, a very rapid increase in the surface concentration must follow. One would therefore expect that the surface concentration would at first increase slowly with the volume concentration and then with increasing rapidity.

That these expectations are realized is shown in the early part of Walker's surface-tension curves.

This explanation seems to fit our case well. Reasoning by analogy, it is probable that at the point  $x$  on each curve, Fig. 10, which is not sharply defined, we have the beginning of the formation of rather large molecule aggregates, or droplets, as in the case of soaps, which have a relatively low osmotic pressure and which chain to the surface with less difficulty than molecules but with more difficulty than the larger aggregates or micellæ that form with increase in concentration. In other words, the increase in size of the micellæ corresponds in a way to an increase in molecular weight of substances forming a homologous series.

Striking support of this theory of the form of the oil in water is in the fact that noticeably turbid or colloidal solutions have true equilibrium or static surface-tension values. That is, emulsions can be circulated to points where the amount of oil, molecules or molecule aggregates, in the surface is in equilibrium with the oil in the volume. As soon, however, as the concentration reaches a point where the aggregate particles become large, in comparison to a molecule, the osmotic pressure or the activity of the micellæ becomes low and they chain easily to the surface, forming noticeable films on the solution. The concentration at which these films occur depends somewhat on the condition of emulsification or, in other words, on the degree of dispersion of the oil.

In one case, it was found impossible to make a stable emulsion by simple agitation at ordinary temperature, 20° C. However, quite stable emulsions of this same oil, namely, Florida Products Co. "C" pine oil, could be effected by the same amount of agitation at a temperature of

60° C. The reduction in surface energy at this higher temperature, which made a higher degree of dispersion possible, is no doubt the explanation. Also a stable emulsion of the same oil resulted when a layer of the oil was allowed to stand on water for several hours. By agitation at 60° C., as much as 25 mg., and by allowing the oil layer simply to rest on the water, as much as 50 to 75 mg. of oil went into stable emulsion with 100 c.c. of water. Perhaps the explanation is that the oil passes into the water phase first as single molecules which later aggregate, made possible by a fluctuating temperature, to form particles or droplets of oil of relatively few molecules in comparison to the droplets formed by mechanical agitation or dispersion. The turbidity may be due to oxidation or hydration of the oil molecules. In concentrations of about 10 mg. in 100 c.c. of water, the solutions were clearly emulsions, as shown by the turbidity. In a Tyndall cone, as little as 3 mg. in 100 c.c. of water showed turbidity.

The ordinary flotation oils in water then are not truly completely soluble (if so, to a very limited extent), but when agitated and mixed with water exist as oil particles ranging in size from that of a single molecule to aggregates of many molecules. From a rather large number of observations, and with a variety of flotation oils, the extent of the solubility could not be given as greater than 5 mg. per 100 c.c. of water or 1 part in 20,000; in most cases it is less than this. This may, however, simulate a true solution in much greater concentration. This is equivalent to 0.3 lb. of the oil in 3 tons of water in flotation practice. It thus appears that in flotation practice pine oils are, in the quantities used, completely soluble or so finely dispersed as to simulate true solutions. The overoiling condition is, possibly, the result of exceeding the concentration at which the oil can simulate a true solution, when there would be present in the pulp many relatively large aggregate molecules, low in osmotic pressure and thus chaining easily to the mineral-water surface when all substances would be oiled.

From the surface-tension curves in Fig. 10, the concentration of this supposed overoiling for the several oils would no doubt occur at the point in the curve where the surface tension ceases to be a function of concentration and when the tension drops very slowly, or not at all, with concentration and finally runs parallel with the concentration ordinate. Practical experience has repeatedly demonstrated that overoiling commences to show at about this concentration.

#### EMULSIFICATION OR SOLUTION WITHOUT AGITATION

That flotation oils are soluble in water or that they diffuse in water in the same manner as a soluble substance is shown in the following experiments: In each of a number of bottles was placed 400 c.c. of distilled water; on the top of the water was poured a layer (about  $\frac{1}{4}$  in. thick) of the

oils as listed in Table 19. Provision was made for withdrawing, from time to time, a part of the water layer for measurement. The bottles were allowed to stand for several days, portions being withdrawn from time to time and surface-tension measurements made. All surface-tension measurements were made at 20° C., but the temperature varied over a considerable range during the standing period. The results obtained are given in the table.

TABLE 19.—*Diffusion of Flotation Oils in Water*

Substance on Water	Surface Tension after Hours of Contact								Mgs. Diffused in 400 c.c. in 240 Hr., Dif- fusion Area 36 Sq. Cm.
	28	48	96	120	144	168	216	240	
Barret Co. No 2 coal-tar creosote. .	71.4	67.0	64.0	65.8	65.9	61.6	64.0	64.8	
Eucalyptus oil. . . . .	52.0	51.8	48.2	45.7	44.5	43.4	43.6	48.6	128 0
Cleveland Cliffs Co No 2 hardwood creosote. . . . .	57.8	53.7	50.0	46.1	45.4	46.2	44.3	44.4	62 0
Sunny South "C" d. d. pine oil. . . . .	49.0	47.2	46.2	45.9	45.6	44.9	44.5	44.5	108 0
Gen. Naval Stores No. 5 s d pine oil. . . . .	44.0	42.7	42.1	42.1	41.6	40.8	39.8	40.0	240 0
Oleic acid . . . . .	65.2	66.2	56.0	61.0	61.0	41.7	49.8	49.0	

The total number of milligrams of the substances diffused in the water was determined by diluting 25 c.c. of the solution with water until its surface tension was well up on the reliable portion of the respective surface tension-concentration curves. Then, from a knowledge of the total number of cubic centimeters of solution and by reference to the curve, a fair approximation of the concentration was determined. All of the solutions appeared turbid after standing an hour or so, and in one or two cases the turbidity was very noticeable at temperatures between 25° and 30° C., while below 10° C. the solution appeared almost clear. As it was thought that possibly only certain soluble constituents of the substances were going into solution, several experiments were devised to check this point, if possible.

Flotation tests, using emulsions of equal strength as prepared above and as prepared by agitation, were made. These showed no significant differences either as to grade of concentrate or recovery. Both were a little higher in the case of the emulsion by oil additions.

By dilution of the emulsions resulting from diffusion, surface tension-concentration points were obtained; these are compared, in Table 20, with points on previously determined curves of the same concentration. The points fall sufficiently close to each other to make it appear as though the oil, and not a constituent of it, is diffusing into the water and that the degree of dispersion in these concentrations by agitation and by diffusion is the same. Mineral adsorption tests using the emulsions

resulting from diffusion gave results almost identical with those obtained in previous tests on emulsions by agitation.

TABLE 20.—*Comparison of Surface Tension of Emulsions of Equal Oil Concentrations, the Emulsions Being Produced by Agitation and by Diffusion*

Substance	Surface Tension of Corresponding Concentrations, Mg. in 100 c c Water				
	10	20	30	40	50
General Naval Stores No. 5 pine oil:					
By addition.....	65.8	60.0	56.0	54.0	52.5
By diffusion.....	65.9	61.2	58.0	54.6	52.6
Sunny South "C" pine oil:					
By addition.....	63.0	58.5	56.0	54.0	52.2
By diffusion.....	63.0	58.5	56.0	54.0	52.1
Eucalyptus oil:					
By addition.....	65.5	60.5	58.5	52.0	50.5
By diffusion.....	65.0	60.4	58.5	52.0	50.5
Cleveland Cliffs hardwood creosote:					
By addition.....	63.0	55.0	55.1	47.5	
By diffusion.....	61.2	65.5	55.0	47.3	

According to the theory that the molecules of such substances as are here dealt with are made up of polar and non-polar groups, which leads to the theory of orientation of molecules at an interface, there seems to be little reason why small aggregates of these molecules should not act as individual molecules. It is natural to assume, in the case of the emulsions formed by diffusion, that as the molecules cluster to form aggregates, the soluble portion, or polar groups, will be held against or drawn into the water phase and that the non-polar, or insoluble ends will be drawn together forming aggregates, as shown in Fig. 16.

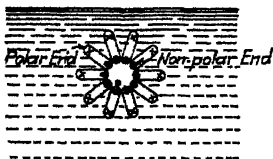


FIG. 16.—HYPOTHETICAL OIL MOLECULE AGGREGATE.

As the active portions of the molecule are probably on the surface of the aggregate, it should behave as a large molecule. Also such an arrangement should give great stability of emulsification. Harkins<sup>41</sup> lays great stress on the fitting of molecules in the surface of droplets and emulsification. He believes that molecular orientation in the interface is a factor that determines the stability of emulsoid particles and also the sign and magnitude of the electromagnetic charge at the surface of the drop. Droplets of substances, such as

<sup>41</sup> *Jnl. Am. Chem. Soc.* (1917) **39**, 592.

benzene or paraffin oil, that have no polar ends, and therefore no attraction for water, would be expected to have no effect on the surface tension of water; this is indeed the case.

Experiments will be given later that throw additional light on the question of the condition of oil in water and probable explanations for oiling of mineral particles will be given.

### COALESCENCE OF LIQUID DROPS

In the light of the new theories of the orientation of surface molecules, the coalescence of liquid droplets forms a most interesting subject. As flotation oils are only slightly soluble, the question is which portion, the soluble, the insoluble (droplets), or both, is effective in flotation. Writers have laid great stress on emulsification in flotation but until the recent paper by Taggart and Gaudin no data have been produced to show whether solutions or emulsions were worked with.

Two kinds of emulsions may exist, or to put it in another way, liquid droplets suspended in a second liquid (water) may be prevented from coalescing by the intervention of films of a third substance and by electric charges, of similar sign, on the droplets.

Liquid droplets of certain substances, such as benzene and paraffin oil, can be emulsified in water only when there is present in the water phase a third substance which is adsorbed in the interface; in other words, substances that have no polar groups in the molecules cannot be emulsified in the absence of a third adsorbable substance. When such an emulsion is produced, the droplets are relatively large and the sign and magnitude of the electric charge on them plays little or no part in the stability of the emulsion. This kind of an emulsion is not met with in the flotation process, for only substances possessing polar groups have so far been successfully used.

Emulsions, the stability of which are dependent on electrical charges on the droplets and not on intervening films, are of special interest in flotation. It should not be understood, however, that in some cases films are not present, for if the pulp contains a contaminant that is rapidly adsorbed at the water-oil interface, we may have a coarse emulsion due to adsorbed films. Such emulsions are unquestionably harmful in flotation; acid may tend to destroy these films and thus be of benefit. But the kind of emulsion obtained, when small quantities of oil (concentration of about 0.0001 per cent.) are agitated in clean water, is particularly important, for the question arises as to the actual part played by the tiny electrically charged oil molecular aggregates. Are these aggregates available to assist oiling of minerals or is only the soluble oil, the amount of which is small, adsorbed? Part of this question will be discussed later but it is proper at this point to consider further the question of emulsion stability and electrical charge. Much has been said on this point but

there is little agreement among writers as to the origin of the electric charge that emulsoid particles are known to carry, and the magnitude of the potential for stability and whether, for complete instability, it is zero or something a little above this.

#### ELECTRICAL CHARGE AND STABILITY OF EMULSION IN RELATION TO FLOTATION

W. Clayton<sup>42</sup> thinks we may accept the usual order of the diameter of emulsion globules as  $10^{-5}$  cm. That the charge on these droplets in water is negative is the common observation; also it has been determined that the potential difference between the oil globules and the continuous medium is 0.03 to 0.06 volt. According to the theory of the polar setting of the oil molecules at the droplet-water interface, the molecules at the oil droplet-water interface will be similarly oriented, therefore the sign of the charge will be the same on all droplets.

If the drops are small, say  $10^{-5}$  to  $10^{-7}$  cm., and if they are all negatively charged, the result will be great stability. Further, if the magnitude of this sign is decreased by the adsorption of a positive ion, the stability of the emulsion will decrease. That in acid solution the stability of an emulsion is decreased is, then, due to the adsorption of the hydrogen ion, which has the effect of lowering the contact potential by neutralization of the negative charge at the polar ends of the oil molecules that are in contact with water. Clayton remarks:

It was until recently thought that when the P.D. decreased to zero, the stability became *nil*, i.e., complete breakdown of the emulsion occurred. However, in 1914, Powis showed that there was a critical potential, *viz.*, 0.03 volt, at which an emulsion is most stable. If the P.D. be now made to decrease, coagulation follows with a velocity which is approximately the same for all values of the potential and the point of complete instability need not necessarily coincide with a zero potential.

That emulsions of the concentration studied in this paper are anything else than emulsions of oil droplets in water as the continuous phase is hardly conceivable. Bancroft<sup>43</sup> advances the theory that the substance of the higher surface tension will be the discontinuous droplet phase. Harkins<sup>44</sup> thinks that such an explanation has no meaning at all, but that the molecular orientation in the interface is the factor that determines the stability of emulsoid particles and also the sign and the magnitude of the electromagnetic field at the surface of the drop.

We have considered emulsions of the type met with in flotation, namely, emulsions of extremely low concentrations of a more or less insol-

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<sup>42</sup> The Modern Conception of Emulsion. *Trans. Chem. Soc. London* (May 31, 1919) 37, 113-19.

<sup>43</sup> "Applied Colloid Chemistry." N. Y., 1921, McGraw-Hill Book Co.

<sup>44</sup> *Jnl. Am. Chem. Soc.* (1917) 39, 593.

ble oil in water where the oil is the discontinuous phase or the droplets, the droplets being so small that the charge (negative) they carry accounts almost entirely for their stability. All substances falling in class 2(b) in very small quantities, from 1 to 30 mg. per 100 c.c. water, should therefore give, when agitated with water, emulsions of this type.

The other type of emulsion, and with which we do not deal in the flotation process, is also one of oil-in-water, or water-in-oil, but the size of drop is so large that the electric charge on its surface has a negligible influence on its stability. Substances of class 2(b) in quantities considerably above 30 mg. per 100 c.c. of water give such emulsions. This type of emulsion is particularly produced when substances of class 3, which have high interfacial energy against water, are agitated with it. Such a substance can be emulsified in water only when a third substance is present. This substance may be finely divided solid colloids, such as water-soluble soaps, or ions. The adsorption of these substances in the interface prevents the droplets from coming in range of molecular attraction with each other and also, through a lowering of the surface tension of the water, prevents the water film from contracting from between the droplets.

As the stability of the type of emulsion of interest to us can be reduced only by the addition of positive ions, which react to neutralize or lower the potential at the interface, the following questions arise:

1. Is the high potential detrimental in flotation and is only the soluble portion of the oil adsorbed by the mineral?
2. Is there a repellent or an attractive action between these negatively charged oil droplets and electrically charged sulfide particles?
3. Is sulfuric acid beneficial through some property to destroy this potential and thereby break up the emulsion? These questions and others will be further considered later.

A few quotations from a recent patent<sup>45</sup> granted to Ridsdale Ellis, which has just come to the writer's attention, will help bring out the importance of these questions as to the electric charge on liquid droplets and on ore particles suspended in water:

Thus, certain types of electrolytes give improved results when added prior to "oiling" and other types better results when added after "oiling." . . . In pure water, an oil globule is strongly charged negatively, a sulfide particle very weakly negatively. Under these conditions, there is a slight electrical repulsion, add a salt of the type of sodium pyrophosphate and the negative charge on both oil globule and sulfide particle will be increased. On the other hand, if a small amount of acid is added, the potential of the sulfide becomes positive while reducing but not reversing the negative potential on the oil, under these circumstances electrical attraction occurs.

In both cases, if the oil globule once comes in contact with the sulfide particle, it will probably spread substantially independently of the sign and magnitude of the

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<sup>45</sup>U. S. Pat. No. 1425185, 1922.



electrical charges on the two materials; but in the first case, it is relatively difficult to get the initial contact of the oil and sulfide and so allow the surface tension forces to come into play, in the other case it is relatively easy. Consequently as sodium pyrophosphate tends to increase the negative charge of both oil and sulfide, it will inhibit "oiling" just as acids aid "oiling" by reversing the sign of the charge on the sulfide.

The observation of the flocculated condition of mineral float when conditions are favorable to best flotation has often been made by those who have done flotation testing. This condition of the mineral floated is no doubt the result of the reaction between negatively charged oil droplets and positively charged mineral particles. For example, colloidal ferric hydroxide can be precipitated by means of an oil emulsion that is negatively charged. Considerable more evidence could be cited to show the importance of these theories of oiling.

#### EFFECT OF WATER-SOLUBLE SOAPS, SODIUM, AND POTASSIUM OLEATE AND PALMITATE IN FLOTATION

Generally, water-soluble soaps, in small quantities, are harmful in flotation. In quantities up to 100 mg. per 100 c.c. water, soap has no effect on the tension of an oil-water interface and yet considerably smaller quantities lower the free surface energy of water to a point (about 40 dynes per cm.) where oil will not spread on it. On a surface of this tension, oil will form into lenticular-shaped globules on the surface of the water. Pine oil on a surface of soapy water behaves just as does Nujol on clean water; that is, pine oil is insoluble in water that contains

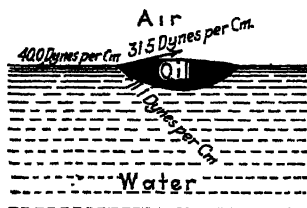


FIG. 17.—SPREADING FORCES IN OPERATION FOR A PINE OIL.

enough soap to prevent its spreading on its surface. At a concentration of soap in water, represented by a surface tension of 40 dynes, the interfacial tension of pine oil is unchanged and the conditions are shown in Fig. 17.

Possibly, at the interface, the concentration of sodium oleate corresponds to a fresh surface, in which case the interfacial tension will not be materially affected for Rayleigh has shown that the tension of a solution of sodium oleate in water for a surface 0.001 sec. old is practically that of water; his figures are:

SUBSTANCE	CONCENTRATION	SURFACE TENSION	TENSION DYNES DYNAMIC
Sodium oleate.....	0.25 per cent. solution	55	79
Sodium oleate.....	2.5 per cent. solution	26	62

It is thus seen that the concentration of soap in water would have to be rather high before the interfacial tension would begin to drop. The quantities required to affect the interfacial tension of an oil-water interface are much greater than has been tried in flotation, but the quantity required to lower the surface tension of water is very small, a fraction of a pound in 3 tons of water will lower it approximately 30 per cent. This effectively prevents frothing or a concentration of the oil on the water-air surface. Water-insoluble soaps, as those of calcium and magnesium, were not found harmful, in the experiments conducted.

### SUMMARY AND CONCLUSION

1. This section considers the reactions at the surface of contact between water and other liquids (oils) that are completely insoluble or only partly soluble in it. The problem is attacked from the point of view of interfacial tension, it being considered that adsorption of a substance or substances in the interface is always accompanied by a change in the value of the interfacial tension.

2. Substances of possible value in flotation are classified into polar (soluble), non-polar or slightly polar (slightly to completely insoluble), and substances composed of both polar (or soluble) and non-polar (or insoluble) groups. Only those substances that contain polar, or soluble, ends have so far found extensive use in flotation. Purely polar substances have been used to a limited extent while non-polar substances have not been used at all.

3. Methods of measuring interfacial tension are discussed; the film method was used in this work. It is believed that this is the first application of the method to interfacial-tension determinations. It is a truly statical method and is especially well suited to the study of interfacial tension as affected by time.

4. Figures for the interfacial tension of a number of common substances in contact with water are given. The interfacial tension of water and oily substances is approximately equal to the difference in the surface tensions of the respective liquids saturated with each other; this is in accordance with Antonov's rule.

5. Contrary to the recorded figures of Harkins and his coworkers, it was found that bases lower greatly the tension at a water-benzene interface and at water-oil interfaces in general. Hydrogen-ion concentration determinations make it appear that this is due to adsorption of hydroxyl ions in the interface, as Bancroft has assumed is the case. The drop-weight method, used by Harkins and his coworkers, gives the tension in expanding, and therefore relatively fresh surfaces, while the film method, used in this work, measures the tension in older surfaces. Surfaces of any age may be investigated; adsorption processes, in general,

are not rapid but take place over periods of several hours; this is particularly true of colloids.

6. Acids and salts in small quantities have little effect on water-benzene and on water-oil interfacial tension in general. Data taken from some work of W. C. M. Lewis show that several salts lower the tension of a hydrocarbon-oil interface. Much stronger solutions were used than are common in flotation practice.

7. Such substances as sodium dibasic phosphate, in the quantities used in flotation, have only small effect on the value of the interfacial tension of oils and water.

8. It is believed that the condition of flotation oils, when agitated and mixed with water, is that of small aggregates of oil molecules ranging in size from one molecule to aggregates of a hundred or so. The size of the aggregates depends on the concentration of oil in water. It is believed that the small droplets are effective in lowering the surface tension of water in some inverse relation to the size of the droplets, and that the stability of emulsions of low concentration is due to electrical charge on the tiny oil droplets and that the sign and magnitude of the charge are important factors in flotation.

9. Flotation oils diffuse into water, if poured on the water surface, as is shown by surface-tension measurements on the water phase. The solutions thus formed are truly colloidal, as is evidenced by a decided turbidity, after standing a couple of hours. Such solutions were also shown to give constant surface-tension values on circulation.

10. Emulsions of oils in water are classified and the factors causing stability considered. It is believed that emulsions, the stability of which are dependent on electrical charges on the droplets and not on intervening films, are of special interest in flotation and further that this type of emulsion is formed when flotation oils are agitated in water.

11. The question of the electrical charge on oil droplets in its relation to oiling of certain mineral particles in a flotation pulp is considered. It is believed that the selective oiling of mineral particles is the result of favorable electrical charges on the oil droplets and on certain mineral particles. Some evidence is given to support this view. When the electrical charge on the oil droplets and the charge on the mineral particles are the same and of sufficient magnitude, there is no oiling of such particles; while if the charges on the oil droplets and on the mineral particles are opposite in sign, oiling of the mineral particles will be greatly facilitated. This seems to be the condition of sphalerite and galena particles in phosphate solutions, where we get flotation of galena and not of sphalerite.

12. Colloids of the water-soluble type, such as soaps, in small quantities lower water-oil interfacial tension only slightly. The tension, however, drops slowly with age of the interface. Amounts up to 1 and 2

per cent. in solution markedly lower the tension; the extent of the decrease is a function of time.

#### SURFACE REACTIONS WITH SPECIAL REFERENCE TO THE ELECTRICAL CHARGE ON MINERAL PARTICLES\*

That solids in contact with a gas or liquid actually have surface energy is generally agreed, but there is no experimental method by which this can be measured. That certain substances, either dissolved or mechanically suspended in water, and ions are adsorbed at the surface of mineral particles, if agitated in the water containing these substances, has been proved experimentally as data given here will show. Granting Freundlich's conception that all adsorption is accompanied by a lowering of the surface energy of the adsorbing phase, this implies a free surface energy at the surface of the solid.

All of the minerals met with in concentration processes, sulfides and those commonly referred to as gangue minerals, possess the power of adsorbing ions and molecules, from aqueous solutions, to a marked extent; the difference in the case of oily substances is in degree only. The sulfide minerals, in general, have considerably larger adsorption capacities than gangue minerals and, for a given constituent, the order of the sulfides, in their adsorption capacities, is very definite. This is also true for gangue minerals. The order of the minerals, in general, is changed if the chemical structure of the "oil" molecules or certain polar groups in the molecules are changed. The presence, in the solution, of a small number of free ions, as a result of dissociation of electrolytes and hydrolysis, will also alter this regular order of things. From what has been said, our problem is strictly one of colloid chemistry; and as this field is so complex, we cannot expect any early and completely satisfactory explanation of the flotation process.

On this point W. C. M. Lewis<sup>46</sup> states: "Colloid chemistry as a science is in a relatively rudimentary state, . . . Our information about colloid systems is disjointed, and we meet with phenomena which in our present state cannot really be explained." He believes, however, that the work of Langmuir and of Harkins marks a radical change in our view of the origin and basis of capillarity. The researches recorded in this paper have been an attempt to analyze the flotation question in its different phases and the experiments on certain of the phases have only opened up possibilities.

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\* R. Jourdan and E. Zange, Fellows in Metallurgy, School of Mines, University of Idaho, are co-authors of this section.

<sup>46</sup> Properties of the Colloid State and Their Application to Industry. *Jnl. Chem. Soc.* (1919).

## SUSPENSIONS OF MINERALS IN WATER

Experiments have shown that many, if not all, colloid particles, and consequently interfaces in general, are electrically charged. The stability of a colloidal dispersion has thus been frequently ascribed to this fact of electrical charge, the removal of the charge being one of the causes of instability and coagulation.

In the flotation process, we deal with particles that range in size from those that will pass a 48-mesh screen (0.295 mm.) to particles so small that they approach true colloidal size. Although the mineral particles are not usually regarded as colloidal suspensions, we are dealing with the same kind of an interface that has been shown, in the case of minerals, to be electrically charged. The charge per unit area is probably of the same order of magnitude as that on the surface of true colloidal particles, but it manifests itself to a less extent, due to the relatively great size of the particle in comparison to the magnitude of the charge. The smaller the particle or the greater the total surface energy of a system, the more active it will be.

It is a little difficult to account for the stability of a suspension in water by any factor other than that of the electrical charge on the particles; there is a mass of evidence that could be cited in support of this theory. Perhaps the best recent contribution relating closely to this subject is that of Mukherjee.<sup>47</sup> Other theories for the stability and flocculation of colloidal suspensions have been advanced; in these Brownian movement and adsorbed viscous films have been stressed. There is little doubt that Brownian movement does play a minor role in both dispersion and flocculation but it does not seem to be capable of very great extension. On the other hand, one has only to work with suspensions of various substances in aqueous solutions of various electrolytes to be convinced of the importance of ion adsorption in its relation to peptization (or deflocculation) and flocculation.

For a suspension of a particle of a given composition and for a given dispersion, the electrical charge will be positive or negative. The particles will be similarly charged with respect to sign and they will exert a strong repellent action on each other, thus preventing their coalescence or flocculation. Permanency of a suspension would therefore be in direct relation to the magnitude or intensity of the electrical charge on the surface of the mineral particles; when this charge is relatively great and the particle is small the particles will be strongly peptized in the suspension medium. Any reduction in the magnitude of this charge would result in decreased stability or in a tendency to flocculate; and the tendency to flocculate would bear a relation to the reduction in the intensity of the electrical charge. When the potential becomes zero, or what is called

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<sup>47</sup> The Adsorption of Ions. *Phil. Mag.* (1922) 44, 321.

the isoelectric point, complete flocculation or maximum instability will be the result. The peptizing or flocculating effect of an electrolyte on a suspension may thus serve to give a qualitative idea of the adsorption of ions on the suspended particles.

#### CAUSE OF ELECTRICAL CHARGE

No satisfactory explanation as to the origin of the charge has been given, but considerable progress is being made in this direction. The older, and what may be called the physical theories of adsorption are giving way to chemical theories of adsorption. The chemical point of view has been put clearly by Langmuir<sup>48</sup> and is being vigorously developed by other investigators. The chemical theory has the advantage that it explains much more satisfactorily the specific nature of adsorption process.

According to Murray,<sup>49</sup> the general opinion as to the cause of the charge is divided under three heads:

1. That the charge is due to ionization of some foreign substance present in the colloid at the moment of formation.
2. That the charge is due to the actual ionization of the colloid itself.
3. That the charge is due to the preferential adsorption at the surface of the colloid of ions present in the dispersion medium.

In support of the third view, which seems to be the one most generally accepted by recent writers, Hardy found that albumin is positively charged in acid solution, negatively charged in alkaline solution, and neutral in pure water. Murray seems to think that this supports the theory that the charge is due to adsorption of hydrogen or hydroxyl ions.

Mukherjee states:

The initial charge of a surface with pure water can be due either to the strong adsorption of an ion of a minute quantity of suitable electrolyte associated with the solid, or to the adsorption of hydroxyl ions from water.

Ridsdale Ellis<sup>50</sup> says:

Whether the metalliferous matter is principally oxide, carbonate, or sulfate, the tendency is for the metalliferous salts in such matter when in contact with water to become hydrated and give off carbonic, sulfuric or other acid which goes into solution in the immediate neighborhood of the surface of the material, and if a sufficient quantity of hydrogen ions are so liberated they give a positive charge to that surface.

These observations are important and seem to be supported by hydrogen ion concentration determinations recorded later in this paper. That the part played by this charge, or potential, that exists at all phase boundaries is of great consequence cannot be denied if we are to accept the modern theories of matter or of the atom, of valence, and of chemical union of elements in general.

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<sup>48</sup> *Jnl. Am. Chem. Soc.* (1916) **38**, 2221; (1917) **39**, 1848.

<sup>49</sup> *Sci. Progress* (1920) **15**, 234.

<sup>50</sup> *Loc. cit.*

The electromagnetic stray field surrounding the atoms exposed at the surfaces of minerals is, no doubt, important and different in intensity for different minerals. Ryschkewitsch<sup>51</sup> says:

The difference of adsorption on gangue minerals and metallic minerals is due to difference of structure. The space lattice of gangue minerals is made up of molecules; that of metallic minerals, of atoms. The metallic minerals, therefore, have a residual valence or unbalanced static force at the surface which is responsible for adsorption.

This statement is interesting but that the space lattice of gangue material is made up of molecules is not generally believed. In support of this view may be given the following statement by Wilson.<sup>52</sup>

It is probable that every substance possesses a certain amount of residual valency at the surface which tends to cause it to combine with substances approaching its surface. As in chemical combination in general such combinations are probably selective.

#### EFFECT OF ELECTROLYTES ON MINERAL SUSPENSIONS IN WATER

That chemicals modify flotation conditions and, when properly used, are of great value in flotation is well known. To obtain the best results, it is necessary to regulate fairly closely the quantity of chemicals used and to use them at the proper stage in the process. The nature of the surface (solid-liquid) reactions bringing about these modifications opens an interesting and important question and one that has received little, if any, attention. Ridsdale Ellis\* states:

With the majority of ores, the most important function of electrolytes in aiding flocculation appears to be the production of favorable electrical conditions. In this respect, it is not the molecules of the electrolyte that are active but the ions produced by the dissociation of the electrolyte when dissolved in an ionizing fluid such as water. . . . In these operations electrolytes may act in four amongst other ways: First, in determining the readiness with which the oil can come into physical contact with the particles of sulfide. Second, in changing the readiness with which the oil after contact with the particles of such sulfide will spread over the surface of the latter and the tenacity with which the oil adheres to the sulfide particle. Third, in determining the readiness with which the gaseous bubbles can come into physical contact with the oiled particles of sulfide. Fourth, in changing the readiness with which the oil after contact with gaseous bubbles will spread over the surface of the latter.

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<sup>51</sup> The Flotation Process of Ore-Dressing. *Chem. Ztg.* (1921) 45, 478.

<sup>52</sup> Theory of Colloids. *Jnl. Am. Chem. Soc.* (1916) 38, 1982.

\* Ellis' patents, copies of which came to the writer's attention after this paper had been written, are unusual in many respects. In these patents a theory of flotation is developed which is similar, in many ways, to that set forth in the present paper. It is what may be called strictly an electrical theory, in which "oiling" of mineral particles is dependent on the attraction of negatively charged oil droplets for positively charged mineral particles as the main factor in bringing about the initial contact between oil droplets and mineral particles. The opposite charges on oiled mineral particles and bubbles are also given considerable importance. The function of chemicals is to control the sign of these electrically charged particles.

The changes produced by electrolytes in any one or more of these ways may be the result of (a) changes in the electrical conditions; (b) chemical changes at the surface of the particle to be floated; (c) changes in surface tension due to adsorption of the electrolyte at the oil-water, particle-water, or air-water interfaces.

Before continuing with this question it is well to mention those chemicals that have marked effects when added to flotation pulps and which have been most successfully used commercially in the process. Of the strong acids, sulfuric acid,  $\text{H}_2\text{SO}_4$ , is the only one that has been used to any extent. In the quantities used (say, from 0.05 to 0.2 per cent. solutions) it is completely dissociated, adding to the water a great excess of hydrogen ions. Its addition to a pulp in many cases results in cleaner concentration, *i.e.*, an increase in the selective action of the oil for the sulfides over the gangue minerals. It is often used to bring about a "reflotative" condition of sphalerite which has been dropped by the addition of a chemical such as sodium carbonate for a selective recovery of the galena.

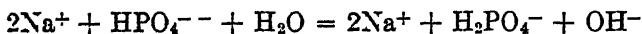
Copper sulfate,  $\text{CuSO}_4$ , which is a salt of a strong acid,  $\text{H}_2\text{SO}_4$ , and a weak base,  $\text{Cu}(\text{OH})_2$ , is no doubt completely dissociated in the concentrations used in flotation and produces an acid solution. Copper sulfate has a marked chemical action. With zinc ores, its use is very beneficial, particularly in floating zinc sulfide (sphalerite) that has been dropped in the lead-flotation cells. With pyrite ores, it is deleterious. The action of copper sulfate on zinc ores is generally believed to be due to the formation of a very small amount of copper sulfide on the surface of the particles of blende, because the zinc being more electronegative than copper tends to replace the latter in solution. The electrochemical action of copper sulfate is further indicated by the fact that the same or similar results can be obtained by inserting a copper plate into the flotation cell. This theory of the action of copper sulfate on sphalerite has never been shown conclusively, experimentally, and therefore may be questioned. This would be an easy point to clear up. In a silver-nitrate solution, sphalerite readily takes on a coating of silver sulfide, as shown by the appearance of the particle.

Experience has shown that a slightly acid pulp is always beneficial to zinc-ore (sphalerite) flotation. Sulfuric acid sometimes gives the desired condition and sometimes both acid and copper sulfates give the best condition. There is a possibility that the hydrogen-ion concentration of the pulp is the important factor. These solutions no doubt charge the sphalerite particles positively, as this seems to be the state of conditions required for the flotation of sphalerite. They are negatively charged in neutral and alkaline solutions.

Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , and sodium dibasic phosphate,  $\text{Na}_2\text{HPO}_4$ , are conspicuous in the field of differential flotation. Each of these, and



particularly the latter, has the property of preventing sphalerite in lead-zinc sulfide ores from floating and of increasing, to a slight degree, the flotation property of the galena. These are salts of a strong base (NaOH) and of a weak acid ( $\text{H}_2\text{CO}_3$  and  $\text{H}_3\text{PO}_4$ ) and in solution they dissociate to give an excess of hydroxyl ions and therefore an alkaline solution. In the dissociation of sodium dibasic phosphate, the hydrogen ion probably associates itself with the  $\text{HPO}_4$  ion to form orthophosphoric acid,  $\text{H}_2\text{PO}_4$ , although the  $\text{HPO}_4$  ion may be dissociated into  $\text{H}^+$  and  $\text{PO}_4^-$  to a very slight extent. Abbot and Bray express the hydrolysis of  $\text{Na}_2\text{HPO}_4$  as follows:



A 0.2 molar solution of the sodium dibasic phosphate is 51.2 per cent. ionized at  $18^\circ \text{C}$ . In amounts commonly used in flotation it is almost, if not completely, dissociated. As will be pointed out later, it is quite probable that sphalerite adsorbs either hydrogen or sodium ions.

Particularly striking separations of sphalerite and galena from lead-zinc sulfide ores can usually be obtained with from 2 to 4 lb. of these reagents per tons of ore. The property to do these things in flotation seems to be specific with these compounds, as it is not generally true for salts of a strong base and a weak acid. For example, potassium or sodium cyanides<sup>23</sup> which give alkaline solutions have not proved of value and, as will be shown, it cannot be due merely to the excess of hydroxyl ions in solution as a result of hydrolysis, as alkaline solutions of NaOH of the same hydrogen ion concentration act differently.

From what has been said above, the following questions arise:

1. Why do such substances as  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_2\text{CO}_3$ , to the extent of from 2 to 6 lb. per ton of ore, hinder the flotation of sphalerite, ZnS, and have practically no effect on the flotation property of galena? Neither of these substances, in the concentrations used, has any appreciable effect on the surface tension of water or on the tension of an oil-water interface.

2. Why for example, does copper sulfate, when added to the aqueous ore pulp from which the galena has been floated by a previous addition of one of the above substances, cause the sphalerite again to become flotative?

3. Is the stability or instability, or the sign and magnitude of the electrical charge on suspensions of minerals in acid, alkaline, or neutral solutions, related in any way to the ease of flotation of these minerals?

In the writings of several persons who have done flotation testing, may be found the observation that the condition of flocculation of the mineral

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<sup>23</sup> U. S. Pat. 1427235, recently granted to Scheridan and Zrizwald of Butte, Mont., calls for the use of a cyanide in conjunction with a caustic alkali or alkali carbonate.

seems to be an essential condition for its flotation. G. J. Young<sup>54</sup> says: "That before a froth can be formed, it is necessary to have conditions present that will permit of flocculation of the mineral particles," such conditions being brought about by the "addition of an electrolyte." Although he fortifies this statement with experiments, C. C. Smith and A. R. Pickett<sup>55</sup> disagree with him and to support their views give tests that are as convincing as those of Young.

H. L. Sulman<sup>56</sup> makes the following unqualified statement on this question:

Oxidized ores of lead and copper without the intervention of any sulfide-filming process are being treated commercially, while recent research has shown that other oxide minerals, such as cassiterite, may be flocculated and thereafter floated; even gangue minerals betray distinct differences in their tendency to float or to remain wetted and sunken. Flocculation of a substance in the state of true suspension is the step antecedent to its flotation, hence the problem in all cases is to secure selective or differential flocculation of the mineral it is desired to float.

Without regard to these statements, which contain no reasons why the condition of flocculation should be beneficial and necessary for flotation, experiments have been made to find, if possible, answers to the above questions.

The experiments of Young mean nothing relative to flocculation, for his solutions were not of the strengths used in flotation. They were so strong in NaOH that both the surface tension of the water and the oil-water interfacial tension were so low that froth flotation could not be expected. However, with this problem we have as a good starting point the fact that the differential separations we have been able to obtain are the direct results of the use of certain chemicals.

#### FLOCCULATION, PEPTIZATION, ELECTRICAL CHARGE, AND FLOTATION

If, as we have assumed, the stability of suspensions of mineral particles in water is due to the electrical charges on the particles, and there is considerable evidence in the literature which favors this hypothesis, we should be able to estimate, roughly, the magnitude of this charge by observing the extent of flocculation or peptization or, in other words, the stability or instability of the suspensions. We should also be able to correlate roughly the flotability of minerals with the degree of stability of their suspensions and thus with the electrical charge on the particle.

Absolute experimental confirmation of such a correlation is difficult because the exact degree of flocculation or peptization of a mineral suspension that has been brought about by the addition of a chemical cannot

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<sup>54</sup> Why Minerals Float. *Eng. & Min. Jnl.* (1918) 105, 1127.

<sup>55</sup> Flocculation in Flotation. *Eng. & Min. Jnl.* (1919) 107, 365.

<sup>56</sup> A Contribution to the Study of Flotation, I. *Min. & Sc. Pr.* (1920) 120, 14.

be determined. Furthermore, a number of factors, such as specific gravity, etc. must be taken into consideration. However, fairly approximate ideas of the effects of chemicals can be had by observing the rate of settling in tubes of given diameter and length. Another way is to observe through a microscope (a binocular microscope was used) the size of the floccule. This method is better when the minerals sphalerite and galena are being compared. The effects of a number of chemicals on mineral suspensions were observed and the results are recorded in Table 21. The mineral powders were produced by prolonged dry grinding in a small porcelain pebble mill; 0.1 per cent. solutions were used in all cases.

TABLE 21.—*Effect of Chemicals on Stability of Mineral Suspensions in Water*

No.	Compound	Sphalerite	Galena	Quartz	Pyrite	Siderite
1	Plain suspension. ....	FW	FW	PW	FW	FW
2	$\text{Na}_2\text{HPO}_4$ .....	PS	PM	PW	FM	PS
3	$\text{Na}_2\text{CO}_3$ .....	PM	FW	PW	FS	PS
4	$\text{Na}_2\text{CO}_3 - \text{Na}_2\text{HPO}_4$ .....	PS	PW	PW	FM	PS
5	$\text{CuSO}_4$ .....	FW	FW	PW	FW	FM
6	$\text{H}_2\text{SO}_4$ .....	FW—	FW	PW		FW
7	$\text{H}_2\text{SO}_4 - \text{Na}_2\text{HPO}_4$ .....	FM—	FW	PW		FW
8	$\text{CuSO}_4 - \text{Na}_2\text{HPO}_4$ .....	FS+	FS	FS	FS	FS
9	HCl.....	FM	FW	FW	FW	PM
10	KCN.....	PM	PW	PW	PM	PW
11	$\text{NH}_4\text{SCN}$ .....	FM—	PW—	PW	FW	PW
12	$\text{SnCl}_2$ .....	PM	PM	PW	FW	PM
13	$\text{CdCl}_2$ .....	FM—	FW	FW—	FW	FW
14	$\text{CdSO}_4$ .....	FM	FM—	FW—	PW	FW
15	K palmitate.....	FW	FW	PW	FS	
16	Na oleate.....	FM+	FM+	PW	FM+	FS
17	Ivory soap.....	FM+	FM	PW	FS	

P, peptize,  
F, flocculate,

W, weak  
M, medium

S, strong

—, minus  
+, plus

The data show how differently the various mineral suspensions are affected by the same chemical and by different chemicals. The difference in the rates of settling or degree of flocculation or peptization is due no doubt to selective adsorption of ions from the water. Suspensions that show greatly increased stability or which are peptized on the addition of a chemical have no doubt adsorbed more ions of the sign of the charge already existing on the surface of the particles. Suspensions that show decreased stability or increased flocculation have no doubt had a part or all of the charge on the particle neutralized by the adsorption of ions of opposite sign.

In several instances the suspensions were stabilized to the extent that no settling of particles was detectable after several hours standing. The most permanent suspension of the sulfide minerals resulted when powdered sphalerite and chalcopyrite were added to very dilute phosphate solutions. The next most permanent suspensions were for sphalerite and chalcopyrite in sodium-carbonate solutions. Both of these chemicals retard greatly the flotation of sphalerite when lead-zinc ores are being treated. They seem to have very little effect, except to increase the recovery, in some cases, on the flotation of the galena. In settling tests some, but no very striking, effect of these two chemicals on galena was observed; the stability was slightly increased in the case of the phosphate solution and slightly decreased in the case of the sodium-carbonate solution.

There is evidence that seems to point to a relation between peptization, flocculation, and flotation. In this particular case, the peptized, or highly electrically charged, condition seems antagonistic to flotation as the flotation of sphalerite is effectively prevented in such solutions. This, however, does not appear to be always the case and it brings up the question of the sign of the charge on the particle and on the oil-molecule aggregate. The best recoveries of galena ore are usually obtained in a slightly alkaline pulp, using particularly  $\text{Na}_2\text{HPO}_4$  or  $\text{Na}_2\text{CO}_3$ , yet galena particles are slightly peptized in phosphate solutions, and strongly flocculated in slightly acid solutions. Galena also floats, but less completely, in acid solutions, i.e., its flotative property is not completely destroyed in acid solution.

That oil droplets in alkaline solution adsorb hydroxyl ions is, probably, not to be questioned for bases lower the interfacial tension of flotation oils against water, and it is thought that, in acid solutions, the hydrogen ion is absorbed. We would then have oil droplets positively charged in acid solution by adsorption of hydrogen ions and negatively charged in alkaline solution by adsorption of negative hydroxyl ions. Then, in the case of sodium phosphate, which gives alkaline solutions, the oil droplets would be negatively charged, which in turn repel negatively charged sphalerite particles and attract positively charged galena particles.

Experiments were designed to determine, if possible, if ions were being adsorbed by the minerals suspensions, particularly in the case of chemicals that show definite effects in flotation.

#### EXPERIMENTS BASED ON HYDROGEN ION-CONCENTRATION DETERMINATION

The acidity or alkalinity of an aqueous solution is a function of the relative number of hydrogen and hydroxyl ions present. Any aqueous solution in which there is an excess of hydrogen ions over the hydroxyl ion is said to be acid, and *vice versa*. True neutrality exists in a solution when the hydrogen and hydroxyl ion concentrations are  $10^{-7.07}$  g.-ions per liter at  $18^\circ\text{C}$ . Such a hydrogen-ion concentration is denoted by  $C_H =$

7.07. In this paper, for greater ease in notation, intensity of acidity is regarded as a function, not of the hydrogen-ion concentration, but of the logarithm of the reciprocal of the hydrogen-ion concentration. Acidity and alkalinity are thus, as is usually done in this kind of work, given in terms of pH; a neutral solution has a pH value of 7.

It is to be noted that the hydrogen-ion concentration and not titratable acidity is desirable. The ordinary titration methods would be of no value in determining the acidity of solutions after treatment with minerals for, in some cases, we work with salts that render the solution acid or alkaline through hydrolysis.

The colorimetric method was considered sufficiently accurate for a reconnaissance of the field, which the work to follow is considered to represent. It is a method much used in biological and soils laboratories and is rapid and fairly dependable. It is not absolute, however, but shows that the hydrogen-ion concentration of an unknown solution is approximately that of a particular standard, which was accurately determined by the more fundamental electrometric method. The colorimetric standards and indicators used were those recommended by Clark and Lubs.<sup>57</sup>

One of the interesting and significant facts brought out in the work on hydrogen ion-concentration determinations was that ordinary laboratory distilled water, unlike tap water, is never neutral but always well within the acid range. This indicates the presence of some substance, such as carbon dioxide, in this distilled water that lacks the buffer action of the suspended material and salts in tap water and brings out a point to be considered when mineral samples are washed with distilled water, previous to treatment in other solutions, and in determining their oil-adsorbing capacities which would no doubt be affected by the presence of the excess of hydrogen ions. Proper consideration of this point was not taken in mineral-oil adsorption experiments recorded later in this paper. However, the experiments were made under similar conditions in this respect.

The method of determining the ion adsorption of minerals from aqueous solutions of salts, acids, etc. by hydrogen ion-concentration determinations is believed to be a powerful tool for looking into the mechanism of controlling agents in flotation. Both the direct and indirect removal or shifting of hydrogen or hydroxyl ions or other ions by adsorption on minerals will be indicated in an increase or decrease in the pH value of the solution. As far as is known the method has never been applied to the study of flotation, notwithstanding that it is widely used in researches on soils and in biological investigations.

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<sup>57</sup> Wm. Mansfield Clark and H. A. Lubs: The Colorimetric Determination of Hydrogen-ion Concentration and its Application in Bacteriology. *Jnl. Bact.* (1917) 2, Pt. I, II, III.

# EXPERIMENTS ON ADSORPTION OF IONS AT SURFACES OF MINERAL PARTICLES

Solutions of a number of substances (electrolytes), of known pH value, were treated with powdered minerals and the hydrogen-ion concentrations again determined after treatment. With regard to the results given in Table 22, it is to be noted that definite changes in hydrogen-ion concentration have resulted from agitation with certain minerals.

TABLE 22.—*Showing Change in Hydrogen-ion Concentration of Various Solutions, When Treated with Different Minerals*

Solution	Strength	Mineral	Grams	Mesh	Blank	Residual Solution
CuSO <sub>4</sub>	20 c.c. N/40 in 230 c.c. dis. water, or equivalent to 0.00032 per cent. solution....	PbS	20.0	—200	4.7	5.0
CuSO <sub>4</sub>	"	FeS <sub>2</sub>	13.0	—200		4.7
CuSO <sub>4</sub>	"	ZnS	10.8	—200		6.0
CuSO <sub>4</sub>	"	SiO <sub>2</sub>	8.0	—200		4.8
Na <sub>2</sub> HPO <sub>4</sub>	20 c.c. N/40 in 230 c.c. dis. water, or equivalent to 250 c.c. 0.33 per cent. solution....	PbS	20.0	—200	7.9	8.5
Na <sub>2</sub> HPO <sub>4</sub>	"	FeS <sub>2</sub>	13.0	—200		7.8
Na <sub>2</sub> HPO <sub>4</sub>	"	ZnS	10.8	—200		7.8
Na <sub>2</sub> HPO <sub>4</sub>	"	SiO <sub>2</sub>	8.0	—200		7.8
NaCl	20 c.c. N/40 in 230 c.c. dis. water, or equivalent to 0.000114 per cent. solution.....	PbS	20.0	—200	4.9	5.1
NaCl	"	FeS <sub>2</sub>	13.0	—200		4.5
NaCl	"	ZnS	10.8	—200		6.3
NaCl	"	SiO <sub>2</sub>	8.0	—200		5.2

NOTE.—Solutions were agitated with minerals for 5 min. and the mixtures were allowed to stand until the suspension had settled well away from the surface when samples were pipetted out for test.

Samples of galena, pyrite, and sphalerite (in quantities as listed in the table) were agitated in 250 c.c. of distilled water taken from a large glass carboy, which contained the distilled water used in these tests. The pH value of the water before and after treatment with minerals is given in Table 23. Then 230 c.c. portions of tap water, to which 20 c. c. N/40 NaCl (c.p. salt) had been added, were treated with the regular quantities of the various minerals with the results shown in Table 24.

TABLE 23.—*Effect of Mineral Particles on pH of Distilled Water*

Sample	pH Values	
	Set 1	Set 2
Galena.....	5.5	5.4
Pyrite.....	4.3	4.3
Sphalerite.....	5.9	5.9
Distilled water.....	5.2	5.2

TABLE 24.—*Effect of Mineral Particles on pH Value of Salt Solution*

Sample	pH Values	
	Set 1	Set 2
Tap water.....	7.1	7.0
Blank (salt solution).....	7.3	7.3
Galena plus blank.....	7.1	7.1
Pyrite plus blank.....	6.5	6.7
Sphalerite plus blank.....	7.3	7.3
Quartz plus blank.....	7.3	7.3

Portions of a sodium-chloride solution, to which had been added sodium hydroxide in sufficient quantity to produce a nearly neutral solution, were treated with various powdered minerals with results as shown in Table 25.

TABLE 25.—*Effect of Mineral Particles on pH Value of NaCl-NaOH Solutions*

Sample	pH Value of Solution	
	Set 1	Set 2
Distilled water.....	4.9	4.9
NaCl-NaOH solution.....	6.4	6.2
Galena plus solution.....	5.4	4.7
Pyrite plus solution.....	4.5	4.6
Sphalerite plus solution.....	6.5	6.2
Quartz plus solution.....	6.5	6.3

Strongly alkaline solutions, 20 c.c. N/40 NaOH in 230 c.c. distilled water, were treated with powdered minerals, with the results recorded in Table 26.

TABLE 26.—*Effect of Mineral Particles on pH Value of Sodium-hydroxide Solutions*

Sample	pH Value of Solutions	
	Set 1	Set 2
Distilled water.....	5.1	5.1
Blank.....	Beyond 10.0	Beyond 10.0
Galena plus blank.....	Beyond 10.0	Beyond 10.0
Pyrite.....	6.3	5.9
Sphalerite.....	10.0	10.0
Quartz.....	Beyond 10.0	10.0
Blank (strength unknown).....	7.4	
Galena plus blank.....	6.6	
Pyrite plus blank.....	4.8	
Sphalerite plus blank.....	6.4	
Chalcopyrite.....	6.6	
Silica (quartz) plus blank.....	6.8	

Solutions of a number of substances and tap and distilled water were agitated in a separatory funnel with benzene and the treated solutions were then drawn out by opening the stopcock after the benzene droplets had risen well away from the discharge. The pH values of the solutions before and after treatment with benzene are shown in Table 27.

TABLE 27.—*Effect of Agitation of Benzene with Various Solutions on pH Value*

Substance in Solution	pH Values	
	Before Agitation with Benzene	After Treatment with Benzene
NaOH.....	7.4	6.6
Na <sub>2</sub> HPO <sub>4</sub> .....	7.8	7.8
H <sub>2</sub> SO <sub>4</sub> .....	4.0	4.6
CuSO <sub>4</sub> .....	4.2	4.7
Distilled water (old).....	5.2	5.8
Tap water.....	6.8	6.9

It should be pointed out that the marked adsorption of hydroxyl ions at the benzene droplet-water interface from the sodium-hydroxide solution is further substantiation of the fact that bases lower the tension at a benzene-water interface.

In Tables 21 to 27, it is assumed that the change in pH value of the solutions on agitation with mineral particles is the result of adsorption of certain ions on the mineral surfaces. However, in the case of pyrite,



definite chemical reaction has taken place in most cases, as the change in pH value of the solutions as a result of treatment with pyrite is greater than can be accounted for by true adsorption. The effect of pyrite on the acidity and alkalinity of water is of considerable importance. Either acid or alkaline solutions are made more acid by treatment with pyrite mineral; therefore if pyrite occurs associated with another mineral (such as galena, for example) which it is desired to float and which requires an alkaline pulp, the presence of the pyrite in the pulp may be particularly undesirable.

Table 27 shows that all the minerals increase quite decidedly the acidity, or decrease the pH value, of a sodium-hydroxide solution. The indications are that all minerals are adsorbing the same ions and presumably the negative hydroxyl ion. It is of interest to note that all the minerals (with the exception of pyrite) and benzene give residual solutions of approximately equal pH values.

Table 22 shows that the alkaline condition resulting from the addition of sodium acid phosphate to water is further increased by treatment with galena and slightly decreased by treatment with sphalerite. Sphalerite is strongly peptized by this chemical while galena is only slightly peptized by it. The reduction in the alkalinity of this solution, when treated with sphalerite, is very slight and of questionable significance. However, that adsorption of certain ions has actually occurred is obvious by the condition of sphalerite suspensions in these phosphate solutions. The suspensions are strongly peptized; that this peptization is due to adsorption of certain negative ions can be shown fairly conclusively. In pure water sphalerite, as are most mineral sulfides, is weakly negatively charged; in acid solutions, this negative charge is neutralized by positive ions and suspensions of sphalerite are flocculated. It seems safe, therefore, to assume that sphalerite suspensions are negatively charged in sodium-phosphate solutions.

The adsorbed ion responsible for the peptized condition of the sphalerite has not been definitely isolated. It may be any one of the following:  $\text{OH}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^-$ , or  $\text{PO}_4^-$ . The adsorption of any one of the last three, which are weak acids, would tend to increase the alkalinity of the solution; that this does not happen is evidence in favor of the  $\text{OH}^-$  ion as the probable ion adsorbed. On the other hand, the alkalinity of the phosphate solution is increased by treatment with galena particles, indicating adsorption of some ion, probably hydrogen or perhaps sodium, by the galena and as there was no noticeable change (slightly less flocculated in phosphate solutions, which agrees with the theory) the inference is that the already positive charge on the galena has been slightly added to by adsorption of more hydrogen or sodium ions. Experiments in which suspensions of galena and suspensions of sphalerite in sodium dibasic phosphate were subjected to a difference of electrical potential showed

that galena particles migrate slowly toward the negative pole and sphalerite strongly toward the positive pole.

For copper sulfate, perhaps the most generally used chemical in flotation, Table 22 shows a decided difference in the adsorptive properties of galena and sphalerite. A very dilute solution had a pH value of 5.0, which was raised to 5.3 and 5.8 when treated with equal surfaces of galena and sphalerite, respectively. Both minerals decreased the acidity but sphalerite more than galena. This is presumably through adsorption of hydrogen ions, or copper ions, but it would appear that the latter would become inactive through association with the hydroxyl ion. However, any adsorption of copper ions would result in decreased acidity if  $\text{SO}_4$  ions formed the second sheet of the adsorbed double electric layer. The acidity is actually decreased in all cases except pyrite, which gives a decided increase in acidity; this no doubt is the result of a true and rather strong chemical reaction.

It is interesting also to note that a weak sulfuric-acid solution was decreased in acidity by treatment with sphalerite but unaffected by treatment with galena; also that ordinary distilled water is acid, which acidity is decreased when agitated with the mineral galena and particularly by sphalerite. Tap water is less acid than distilled water and it passes to alkaline when treated with galena and sphalerite.

The foregoing may be summarized as follows:

1. Salts of strong bases, particularly sodium and potassium hydroxides, and of weak acids, particularly phosphoric and carbonic, dissociate in aqueous solutions and hydrolyze to give weakly alkaline solutions.

2. Salts of weak bases, particularly copper hydroxide, and of strong acids, particularly sulfuric, dissociate and hydrolyze to give acid solutions.

3. All the sulfide minerals are flocculated and quartz peptized in weak sodium-hydroxide solution. In every case, the acidity of the treated solutions has been increased, presumably through the removal of sodium hydroxide, by adsorption, either the sodium ion or the hydroxyl ion forming the adsorbed layer. That it is probably the  $\text{OH}^-$  ion that is adsorbed would seem to follow from the fact that it is known that nearly all suspensions are negatively charged in alkaline solutions.

4. In a sodium dibasic phosphate solution, galena is weakly peptized, pyrite strongly flocculated, and sphalerite, chalcopyrite and quartz strongly peptized. Galena increases the alkalinity, sphalerite and chalcopyrite just slightly decrease it, while pyrite and quartz noticeably increase the acidity of the solution. Presumably galena adsorbs hydrogen or sodium ions; sphalerite and chalcopyrite adsorb hydroxyl ions, to a slight extent, if at all, while pyrite and quartz adsorb them strongly. In the case of pyrite, there is perhaps a solution effect.

5. All the minerals, except quartz, are flocculated in a weak sulfuric-acid solution. Galena does not affect the pH value of the solution while pyrite increases markedly the acidity, and sphalerite, chalcopyrite, and quartz decrease the acidity. Presumably, galena adsorbs neither ion to any marked degree; the other minerals, except pyrite, adsorb hydrogen ions.

6. All the minerals, except quartz, are flocculated in copper-sulfate solution. Galena decreases slightly the acidity of the solution and all the other minerals (except pyrite, which increases the acidity) decrease the acidity noticeably. The ions adsorbed are presumably either hydrogen or copper.

7. For distilled water, which contained some dissolved  $\text{CO}_2$ , the acidity is decreased by galena and sphalerite and increased by pyrite. In these solutions, suspensions of galena and sphalerite appear to be slightly flocculated, indicating adsorption of  $\text{H}^+$  ion, thereby neutralizing to some extent the negative charge carried by these particles in distilled (carbon-dioxide free) water.

8. Galena, pyrite, and sphalerite are slightly flocculated in tap water, while chalcopyrite and quartz are peptized in it. Pyrite increases decidedly the acidity of tap water, while the other minerals increase the alkalinity and bring the solutions into the alkaline range of indicators.

That minerals possess marked selective adsorption of ions from aqueous solutions of various salts and acids is borne out by the foregoing experiments. That the nature and intensity of the electrical charges on the different mineral particles in the same solutions are different seems entirely unquestionable; and that the intensity of the charge is dependent on the hydrogen-ion concentration of the solution seems also to be borne out by these experiments. A number of references may be cited to show the importance of the hydrogen-ion concentration in settling of clay suspensions and in the control of colloidal solutions. Suspensions of various substances in water seem to have maximum and minimum stability at different and definite H-ion concentration; *i.e.*, electric charges on the particles reach a maximum intensity or are entirely neutralized at definite H-ion concentrations. In a paper dealing with the factors affecting the H-ion concentration of natural waters and the influence of H-ion concentration on suspended matter, Wolman and Hannan<sup>58</sup> say as follows:

The standardization of rates of filtration of depths of sand beds and size of sand grains has been determined in most cases without reference to the reactions and electrical signs of either the water or the material suspended therein. In this connection, it need only be recalled that many substances when suspended in water become negatively charged, with the intensity of the charge increasing when the concentration of the hydroxyl ion becomes greater. In particular clay particles and bacteria are usually negative, while it is believed that alumina used for the mechanical filtration is negative when the pH of the solution is greater than 7.5 (Sorensen's scale). *Naturally*

<sup>58</sup> *Chem. & Met. Eng.* (1921) 25, 502.

*the negative charges of such substances are influenced greatly when the hydrogen-ion concentration is increased or lowered.\* . . .* The volume of granules is very variable as is especially a function of the reaction of the medium. One ought, therefore, to take account of this reaction, all the more because upon it depend the sign and the size of the electrical charge. Perrin has shown in effect that every membrane in contact with an alkaline solution is charged with negative electricity. If the solution is acid, the membrane is positive. Quincke further demonstrates that if we cause alkaline water to pass through a capillary tube or a filter of sand or of gelatine, we obtain the positive charge of the water toward the outlet, while at the entrance the negative electricity has accumulated.

The following quotation, from page 1257 of *Chemical and Metallurgical Engineering* for Dec. 27, 1922, bears directly on this question.

The rate of settling of clay is thought to be an important matter in connection with the use of clays as a filler in paper making. The rate of settling of clay in a medium is to a certain extent dependent on the hydrogen-ion concentration of the suspending medium. The rate of settling of six clays has been studied over a wide range of hydrogen-ion concentrations. For each clay-water mixture, there is a definite hydrogen-ion concentration at which the rate of settling will be a maximum, and also a definite concentration at which this rate is a minimum. In the purification of clay, these two points should be known in order to effect the separation of clay particles from quartz and mica particles most efficiently.

In a preliminary report<sup>59</sup> of the effect of H-ion concentration on the precipitation of mastic and gamboge sols by acids and salts, Tartar and Gailey state that acids cause precipitation at the same H-ion concentration and certain salts precipitate the sols at the same concentration provided the H-ion concentration is kept approximately constant. Also that the precipitation values of the salts employed vary as the concentration of the colloid at the same H-ion concentration. These authors conclude that the ion having the same charge as the colloid is without influence in the cases studied.

The present writers believe that this investigation, in which the relation of hydrogen-ion concentration to flotation concentration is considered, is capable of great expansion. If in these experiments the H or OH ions themselves are not actually adsorbed, they are controlling factors in the adsorption of other ions. Neutral salts have found little, if any use, in flotation-concentration practice. The chemicals that have been of practical aid in the commercial process are those that ionize in water and through hydrolysis give either an excess of H or OH ions to the solution and, further, the amount of any salt used must generally be under close control. This suggests that the factor we have been actually controlling is that of H-ion concentration. Commercially, H-ion control has made considerable headway in several important fields. This may prove, with further work, to be a method suitable for the control of commercial flotation operations.

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\* Italics are the authors.

<sup>59</sup>*Jnl. Am. Chem. Soc.* (1922) 44, 2212.

## SUMMARY AND CONCLUSIONS

1. This section had, for its purpose, a consideration of the reactions at the surface of contact between a liquid (aqueous solution) and a solid (mineral particles), with the object of correlating such factors as electric charge on mineral particles and stability of mineral suspension in water, with their flotation characteristics.

2. In the flotation process, we deal with particles that range in size from those that will pass a 48-mesh screen (0.295 mm.) to particles so small that they approach true colloidal size. It is considered that the individual mineral particles of a suspension in water are charged with either positive or negative electricity and that this charge is due to adsorption of certain ions in solution. The states of flocculation and peptization of suspensions are attributed, in the main, to ion adsorption. The degree of peptization affords a method of determining roughly the magnitude of the electric charge on the individual particles of a suspension. Settling tests, in conjunction with hydrogen-ion concentration determinations of solutions before and after treatment with mineral particles, afford a fairly good method of determining the nature of the ions adsorbed on the mineral surfaces.

3. The peptization and flocculation action of various chemicals on suspensions of different minerals in water have been observed, with the following results: (1) The stability of a given mineral suspension in water is generally either increased or decreased if small amounts of a substance capable of giving a change in hydrogen-ion concentration are dissolved in the water. (2) In the cases investigated, practically all mineral suspensions in water are increased in stability in solutions having a pH value greater than 7; and decreased in stability, showing a tendency to flocculate, in solutions having a pH value below 7. The change generally is particularly noticeable in the case of the sulfide minerals. In the case of gangue minerals, the changes due to electrolytes are much less noticeable and this rule holds less closely. (3) Generally speaking, in the cases investigated, the pH value of slightly acid solutions is increased by treatment with various minerals; and slightly alkaline solutions are reduced in pH value on treatment with various minerals. Pyrite is always an exception to this rule and galena is an exception in one or two cases. Pyrite reduces the pH value in all cases and suspensions of pyrite are nearly always flocculated no matter what the solution. (4) Generally speaking, the hydrogen-ion concentration appears to be the important factor in regard to the magnitude and sign of the electric charge on mineral suspensions.

4. From a determination of the pH values of a number of electrolytes before and after treatment with benzene droplets, it is shown that the pH value is decreased in the case of solutions of pH value above 7 and increased in the case of solutions of pH value below 7. As various other investiga-

tors have shown that liquid droplets are positively charged in acid solutions and negatively charged in alkaline solutions, we have evidence that droplets adsorb  $H^+$  ions from acid solution and  $OH^-$  ions from alkaline solutions.

5. In a weak sodium-phosphate solution, indications are that galena adsorbs one ion and sphalerite another. Both minerals are peptized by this chemical, galena only slightly and sphalerite strongly, indicating an electric charge on each, but of opposite sign as galena increases the alkalinity of the solution while sphalerite slightly reduces it. The particles of galena are positively charged while sphalerite particles are strongly negatively charged. This affords a possible explanation of the part played by this chemical,  $Na_2HPO_4$ , in the differential flotation of galena and sphalerite. It would appear that the presence of negative electricity (ions) on sphalerite particles and on oil droplets effectively prevent oiling of the sphalerite through repulsion of like charges, while galena is readily oiled due to attraction of negatively charged oil droplets for positively charged galena particles.

6. Peptization of a mineral in flotation does not indicate necessarily either an antagonistic or a receptive condition of the mineral to flotation. Neither does flocculation. But peptization as a result of an electric charge on the mineral of a sign similar to that on the oil micellæ seems to indicate a condition antagonistic to flotation while peptization as a result of an electric charge of a sign opposite to that on the oil droplet is seemingly a most desirable condition.

7. Flocculation means a low or zero electric charge on the mineral particles. When the mineral appears flocculated, it may be positively or negatively charged; that quartz adsorbs hydrogen ions in acid solutions does not mean that the charge on the particles is positive but rather that it is slightly negative, if anything, as there is no doubt a small amount of the negative charge on the particle that is unneutralized by the adsorption of hydrogen ions; however, it may go past the isoelectric point and become charged with the sign of the ion adsorbed.

8. In the case of quartz and benzene, quartz is much more stable in alkaline solutions than in acid and the adsorption is presumably of hydroxyl in all cases. The magnitude of the charge is greater in alkaline than in acid solutions and benzene is more easily emulsified in alkaline than in acid. The charge is possibly negative in both cases but much stronger in alkaline than acid solutions, for most of the negative charge has been neutralized in acid solutions by adsorption of hydrogen ions. In fairly strong acid solutions, the droplets become positively charged.

9. The flocculation often observed in flotation testing, when the condition is right, is probably due to a coagulation of, say, negatively charged oil droplets or micellæ with positively charged mineral particles, as in the

case with galena when phosphate is used. The galena collects on the surface of the pulp in a coagulated mineral-oil mass, but the pulp does not appear flocculated but, rather, peptized.

10. When a differential separation of minerals by flocculation is possible, the experiments here recorded make it appear that it is due to the adsorption by the minerals of ions of opposite sign, which causes the mineral particles to be positively or negatively charged. The mineral charged with electricity of a sign opposite to the sign of the charge on the oil aggregates will become "oiled," while the mineral charged with electricity of the same sign as that of the oil aggregates will not become oiled.

11. In this work, time did not permit experiments of a more quantitative nature. Experiments that would give H-ion concentration at which different minerals suspension had maximum and minimum stability would be of considerable interest. In general, the writers believe that the line of investigation followed has opened a field that will permit a scientific investigation of the causes of flotation that should be of considerable value in practice. In flotation testing, it has been shown that the hydrogen electrode is of great help in obtaining exact conditions of flotation pulp.

#### SURFACE REACTIONS WITH SPECIAL REFERENCE TO THE ADSORPTION OF FLOTATION OILS BY MINERAL SEPARATION

The film method of measuring surface tension that was used throughout this investigation has its limitations. Substances that lower the surface tension of water very little or not at all cannot be investigated; but as such substances have not found any application in flotation concentration there is no particular need for any investigation of these substances in flotation. Experience seems to show that a substance (oil or other contaminant) to be of value in flotation must not only tend to lower the water-air interfacial tension, but it must tend to envelop the mineral particle.

The accuracy of the surface-tension method of measuring adsorption appears to hinge entirely on the question of the condition of the oils when agitated and mixed with water. Wood oils, chiefly pine oils, were mostly investigated; although camphor and eucalyptus oils and a number of pure substances were investigated to a limited extent.

If every milligram of such oil added and mixed with water is effective in lowering its surface tension and if the decrease is not caused by some particular constituent of the oil that is more soluble than the remaining portions, and if it is not caused by the solution of part of the oil, the surface-tension method of determining the amount of

any particular oil in and removed\* from a mixture of it in water should be quite accurate.

The condition of flotation oils in water has already been considered. The indications were that many commercial flotation oils are only very slightly soluble in water and that the condition of the oil in water, in the concentrations investigated, is that of droplets, or molecular aggregates ranging in size from one or two molecules to aggregates of large groups of molecules; also that the molecule aggregates are effective in lowering surface tension and that the stability of the solution in the very low concentrations is caused by the electrical charge on the droplets.

#### PROCEDURE FOLLOWED AND CONDITIONS OF EXPERIMENTS ON ADSORPTION

The minerals galena, sphalerite, pyrite, chalcocite, chalcopyrite, siderite and quartz were used as the adsorbents in the work to be outlined. Galena and siderite were from the Bunker Hill & Sullivan mine, at Kellogg, Idaho; chalcocite from Butte, Mont.; chalcopyrite from Globe, Ariz., sphalerite from Missouri; and the quartz was clean sea sand obtained from the roads department of the University of Idaho. Perfectly clean specimens only were used. They were crushed carefully to give a maximum number of particles of a given size; the size of particle generally used was that which passed through a 28- and remained on a 35-mesh screen.

In determining adsorption capacities or rates of adsorption of the different minerals, either equal volumes were used or the minerals were weighed out in such portions as were calculated to represent approximately equal surface areas; the area in all cases, except when specified, was 314 sq. cm. as nearly as could be calculated. No doubt the actual amount of surface in any case was only approximately determined. If in the particles of mineral, especially in the case of galena, there were no cleavage planes sufficiently open to take up oil by capillary action, there would still be room for considerable error in calculation of total surface, because of difference in the shapes of particles. Galena breaks or fractures easily

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\* In view of the experiments recorded, it is best here to speak of the oil emulsified in the water as "removed" or collected by the mineral and not adsorbed by the mineral; as the amount of oil taken up by the mineral particles is shown to be equivalent to a film many molecules deep, true adsorption could account for films to exceed not more than a couple of molecules deep. However, this statement is not intended to convey the idea that true adsorption of oil by mineral particles does not actually take place. There is undoubtedly, first, true adsorption of the portion of the oil existing in the water as individual molecules, as seems to be shown by the work of Taggart and Gaudin, followed later by the spreading of oil droplets on the oily surface of the mineral particles. There may not be even a spreading of the oil droplets on the mineral particles, it may be simply a sort of a coagulation action between droplets and mineral particles.



into particles that are more cubical than any other shape, while siderite breaks into particles of a more slivery nature. In general, it is believed that the actual amount of surface used was more than that given by calculation.

The practice was to circulate the emulsion used. Emulsions of concentrations falling on the more or less flat portion of the surface tension concentration curves were scarcely ever used, as data by the surface-tension method on emulsions of these concentrations were considered of doubtful reliability. As has been stated, only emulsions of very low concentrations can be circulated to constant surface-tension values.

Agitations were usually carried out in Erlenmeyer flasks, which were rinsed with the emulsion to be tested before the mineral was added in order to take care of any adsorption of the contaminant oil by the glass. Dry mineral previously washed with distilled water was generally used. The time of agitation, which was effected by hand, was 2 min. unless otherwise stated.

The temperature was not under as good control as was desired, but tests were made usually at 20° C. When immediate comparison of a series of experiments was made, the temperature was the same for individual tests of the series.

After the agitation was completed, 50 to 75 c.c. of the treated emulsion was drawn out with a pipette and discharged into a suitable vessel for the surface-tension measurement. The practice was to circulate the emulsion in the vessel by means of a pipette until the tension in the surface film had reached a constant point. Emulsions after treatment with mineral came more quickly to constant surface-tension values than did the original emulsions. The possible significance of this fact will be considered later.

If surface tension-concentration curves for the oils used in the experiment were available, reference was made to them and the number of milligrams of oil removed by the mineral was determined from them. If curves were not available or had not been determined, the increase in surface tension of the residual over the original emulsions gives a fair idea of the relative adsorptive capacities of the minerals for that oil.

#### ADSORPTION OR REMOVAL OF OILS FROM WATER BY MINERALS

The tests recorded here represent only a small portion of the large number made. Much time was spent in determining conditions under which reasonably concordant results could be obtained. Table 28 gives data for seven minerals common in flotation practice and for eleven common flotation oils. The second column shows the concentration of the original emulsion and the third column the surface tension of the original emulsion. The increase in surface tension of the emulsion after

TABLE 28.—*Adsorption of Oils from Water by Minerals*

Substance	Mg. Oil in 100 c.c. Water	Surface Tension of Emul- sion	Dynes Increase in Surface Tension when Treated with 814 Sq. Cm. Mineral Surface						Milligrams of Oil Adsorbed on 100 Sq. Cm. of Mineral Surface								
			PbS	Cu <sub>2</sub> S	FeS <sub>2</sub>	CuFeS <sub>2</sub>	ZnS	FeCO <sub>3</sub>	SiO <sub>2</sub>	PbS	Cu <sub>2</sub> S	FeS <sub>2</sub>	CuFeS <sub>2</sub>	ZnS	FeCO <sub>3</sub>	SiO <sub>2</sub>	
General Naval Stores No 5 s. d pine oil. ....	13.95	62.2	2.0		0.7	1.0	0.7	0.0	0.0								
Pensacola Tar and Turp. Co No. 400 wood creosote.....	10.90	56.5	2.5	1.4	2.2	1.6	0.2	0.4	0.0								
Hunter Johnson Co. No. 259 pine oil.....	10.00	60.2	2.1	1.1	0.8	0.0?	1.1	0.1	0.7								
Florida Products Co. "C" pine oil.	10.10	63.0	2.0	0.4	1.1	0.3	0.9	0.0	0.2								
Port Orford cedar oil.....	7.3	59.5	3.6	1.8	1.2	1.1	0.5	0.1	2.3?	1.00	0.20	0.10	0.10	0.40	0.00		
Burgess Co. green camphor oil.....	9.7	51.7	2.1	1.2	1.4	1.9	1.5	1.0	0.8	1.00	0.73	1.03	1.33	0.716	0.61		
Barret Co. No. 2 coal-tar creosote. Cleveland Cliffs Co. hardwood creosote No. 1.....	15.45	68.8	2.5	1.0	1.0	1.0	1.0	1.0	1.0								
.....	10.4	60.3	2.9	0.8	1.7	2.0	0.7	0.3	0.5								
Eucalyptus oil.....	14.4	61.7	2.5	2.0	2.8	2.6	2.0	2.0	1.8	1.50	1.75	1.08	1.53	1.30	1.24	1.14	
Eucalyptus oil .....	18.0	60.5	2.5	2.7	3.1	3.0	2.2	1.3	1.4								

treatment with the various minerals is given, also the number of milligrams of oil removed from the emulsion by 100 sq. cm. of mineral surface. No surface tension-concentration curves were made for oils for which these values were not given.

The outstanding fact in the table is that galena causes the greatest increase in surface tension, and therefore collects the most oil per unit of area, in all cases except for eucalyptus oil, for which it stands fourth in order of quantity of oil collected. The mineral occupying second place the greatest number of times is chalcopyrite, which is followed by pyrite, chalcocite, sphalerite, quartz, and siderite in the order written. Sphalerite is always well down in the order of adsorptive capacity; quartz and siderite increase the surface tensions of the emulsions only slightly, in comparison to the sulfides or the more flotative minerals. The order, in general, compares well with the ease of flotation of these minerals as shown from experience.

#### THICKNESS OF OIL FILMS COLLECTED ON MINERAL SURFACES

The thickness of the films of oil surrounding the mineral particles can be approximately determined, by the equation  $TND = W$  where  $T$  = thickness of film, in centimeters;

$N$  = number of square centimeters of mineral surface;

$D$  = density of oil adsorbed;

$W$  = weight of oil, in milligrams, collected by  $N$ .

$N$  and  $W$  are known and  $D$  may be taken as unity.

For green camphor, Sunny South "C," and eucalyptus oil, the thicknesses of the films collected by the minerals are listed in Table 29. Assum-

TABLE 29.—*Thickness of Oil Layers Collected from Oil-water Emulsions by Minerals*

	Green Camphor Oil cm.	Sunny South "C"	Eucalyptus Oil
Galena.....	$1.6 \times 10^{-5}$	$1.0 \times 10^{-5}$	$1.56 \times 10^{-5}$
Chalcocite.....	$0.73 \times 10^{-5}$	$2.0 \times 10^{-5}$	$1.75 \times 10^{-5}$
Pyrite.....	$1.03 \times 10^{-5}$	$4.0 \times 10^{-5}$	$1.68 \times 10^{-5}$
Chalcopyrite.....	$1.33 \times 10^{-5}$	$1.0 \times 10^{-5}$	$1.53 \times 10^{-5}$
Sphalerite.....	$0.716 \times 10^{-5}$	$4.0 \times 10^{-5}$	$1.30 \times 10^{-5}$
Siderite.....	$0.710 \times 10^{-5}$		$1.24 \times 10^{-5}$
Quartz.....	$0.63 \times 10^{-5}$	$0.8 \times 10^{-5}$	$1.14 \times 10^{-5}$

ing that the length of the molecules of the oils adsorbed are of the order of those of castor and olive oil, films of which have been very carefully determined by Raleigh and by Marcelin to be  $1.3 \times 10^{-17}$  and  $1.0 \times 10^{-7}$ , respectively, we are led to the conclusion that the films on the minerals are from 10 to 100 molecules deep.

TABLE 30.—*Adsorption of Pure Substances by Mineral, 20° C.*

Substance	Concentration	Sur- face Ten- sion	Increase in Surface Tension After Treatment						Milligrams Oil Adsorbed in 100 Sq. Cn. Mineral Surface					
			PbS	Cu <sub>2</sub> S	FeS <sub>2</sub>	CuFeS <sub>2</sub>	ZnS	SiO <sub>2</sub>	PbS	Cu <sub>2</sub> S	FeS <sub>2</sub>	CuFeS <sub>2</sub>	ZnS	SiO <sub>2</sub>
Oxalic acid, 2(COOH).....	N/5	65.0	2.3	0.0	0.5	0.2	0.5	0.4						
Formic acid, H(COOH).....	N/1	63.0	0.0		2.2	6.9	0.9	2.2						
Acetic acid, CH <sub>3</sub> COOH.....	N/5	62.8	2.2	1.4	2.4	2.2	1.5	1.4	0.16					
Propionic acid, CH <sub>3</sub> (CH <sub>2</sub> )COOH.....	96 mg./100 c.c. H <sub>2</sub> O	71.1	0.1	0.7	0.5	0.7	0.6	0.5						
Butyric acid, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH.....	100 mg./100 c.c. H <sub>2</sub> O	70.0	0.5	0.7	0.1	0.6	0.2	0.2						
Heptylic acid, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> COOH.....	10.6 mg./100 c.c. H <sub>2</sub> O	64.5	0.5	3.8	0.6	2.0	0.5	0.5	0.31	1.46	0.38	0.76	0.25	0.25
Caprylic acid, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH.....	2.6 mg./100 c.c. H <sub>2</sub> O	66.3	2.0	4.5	0.8	2.3	1.7	1.2	0.24	0.57	0.10	0.29	0.20	0.15
Caproic acid, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH.....	15.5 mg./100 c.c. H <sub>2</sub> O	69.1	0.3	1.5	0.3	0.7	0.2	0.1						
Iso-caproic acid, (CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>4</sub> COOH.....	40 mg./100 c.c. H <sub>2</sub> O	66.4	0.7	1.6	0.6	0.7	0.8	0.6						
Succinic acid, COOH CH <sub>2</sub> CH <sub>2</sub> COOH.....	100 mg./100 c.c. H <sub>2</sub> O	71.9	0.4			0.1	0.0	0.0						
Butyraldehyde, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO.....	23 mg./100 c.c. H <sub>2</sub> O	56.7	1.1	2.0	1.7	2.4	2.5	2.1						
Heptaldehyde, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CHO.....	9.6 mg./100 c.c. H <sub>2</sub> O	53.3	0.4	0.5	0.9	0.7	0.7	0.3						
Methyl alcohol CH <sub>3</sub> OH.....	80 mg./100 c.c. H <sub>2</sub> O	Scarce	ly any	lowering of	surface	tension								
Propyl alcohol, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH.....	80 mg./100 c.c. H <sub>2</sub> O	Scarce	ly any	lowering of	surface	tension								
Butyl alcohol.....	45 mg./100 c.c. H <sub>2</sub> O	68.4	0.5	0.8	0.9	0.8	0.0	0.2						
Octyl alcohol, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> OH.....	4.9 mg./100 c.c. H <sub>2</sub> O	56.5	1.1	1.1	2.1	1.9	2.1	2.3						

NOTE.—Lauric and stearic acids are solids at ordinary temperatures; nitro, tartaric and octane solutions gave unsatisfactory readings.

Similar calculation for two pure compounds (the data used as the basis for the calculation were taken from Table 30) gave the results shown in Table 31. The thickness of the film again ranged from 10 to

TABLE 31.—*Thickness of Layers of Pure Substances Adsorbed by Minerals*

	Heptylic Acid $\text{CH}_3(\text{CH}_2)_5\text{COOH}$	Caprylic Acid $\text{CH}_3(\text{CH}_2)_6\text{COOH}$
Galena.....	$0.31 \times 10^{-8}$	$0.24 \times 10^{-8}$
Chalcocite.....	$1.46 \times 10^{-8}$	$0.57 \times 10^{-8}$
Pyrite.....	$0.36 \times 10^{-8}$	$0.10 \times 10^{-8}$
Chalcopyrite.....	$0.76 \times 10^{-8}$	$0.29 \times 10^{-8}$
Sphalerite.....	$0.25 \times 10^{-8}$	$0.20 \times 10^{-8}$
Siderite.....		
Quartz.....	$0.25 \times 10^{-8}$	$0.15 \times 10^{-8}$

100 molecules. The copper minerals show the highest adsorption, which possibly may be due to slight solubility of the copper mineral in these weak acids.

#### ADSORPTION OF PURE ORGANIC SUBSTANCES BY MINERALS

The chemicals used were of the best grades, all being procured from the Eastman Kodak Co. The object of the work on pure organic substances was to determine if any relation existed between molecular structure of various solutes and adsorption by minerals. Substances of the formic-acid series having the polar group  $\text{COOH}$ , aldehydes having the polar group  $\text{CHO}$ , and alcohols having the polar group  $\text{OH}$ , and a few other miscellaneous substances were tested. The nature of the work required considerable routine work and before any conclusions of any importance can be drawn, a large mass of carefully obtained data must be in hand. The investigation was not carried far enough for us to draw any conclusions that pertain to adsorption, except as it showed that all minerals show adsorption for surface-tension lowering substances.

In such an investigation, solutions of equal molecular concentration should be used if important comparisons are to be made; but it was impossible to meet this requirement, using the surface-tension method, because of the different surface-tension lowering properties of the substances. For example, as little as 10.6 and 2.6 mg. of heptylic and caprylic acid, respectively, in 100 c.c. of water lowered its surface tension greatly while the shorter chained propionic and butyric acids had little effect on the surface tension when as much as 100 mg. were dissolved in 100 c.c. of water. The same thing is true of the aldehyde and alcohol series. The work was therefore discontinued but the substances tested

and the observations made are recorded in Table 31. The apparent high adsorption in many cases is no doubt due to slight solubility of the mineral in the solution. This was clearly the case with the copper minerals in some of the solutions. It was necessary, in the surface-tension measurements of these solutions, to treat them similarly to emulsions of flotation oils in water, in order to obtain constant readings. That is, it was necessary to circulate the solutions, using a 100 c.c. pipette, a number of times to obtain the true static or equilibrium tension. The tensions were always high at the initial reading. The time required to reach constancy was always less for true solutions than for emulsions.

Taggart and Gaudin<sup>60</sup> were apparently able to obtain satisfactory (presumably constant) surface-tension readings, using the film method in their work on adsorption from solutions. Their work also indicates, in the case of true solutions, that minerals adsorb oil on their surfaces equivalent to a layer one molecule thick. In the case of flotation oil-water emulsions Taggart and Gaudin think that it is useless to try to determine adsorption from emulsions by the use of the film method; they state:

The first tests were made with emulsions of pine oil (G.N.S. No. 5), Cleveland Cliffs, No. 1 (hardwood creosote), and Barrett No. 4, (coal-tar creosote). These oils are typical of their classes. The results were erratic and unsatisfactory, caused, without doubt, by greasing of the knife-edge in the surface-tension determinations on the original emulsion. The Erlenmeyer-flask adsorption method was used. The results, though poor, are included to give an idea of their erratic character and to impress the fact that it is useless, with this apparatus, to try to determine adsorption in emulsions. See Tables 8 and 9. An attempt was made to duplicate exactly Fahrenwald's tests on adsorption with emulsions of hardwood creosote; our results disagree widely with his. Both sets are tabulated in Table 10, for comparison.

In their Table 10, their data show negative adsorption of oil by three of the five minerals tested and a small positive adsorption by the other two minerals; the average difference in the surface tension of the emulsions before and after treatment with the minerals being 0.05 dyne per cm. The data of Fahrenwald<sup>61</sup> show positive adsorption in all cases, the average difference in the surface tension of the emulsions before and after treatment with minerals being 4.4 dynes per centimeter.

Since Taggart and Gaudin did not take into consideration the factor of time on the value of the surface tension of emulsions, their readings may easily vary several dynes on solutions both before and after treatment with minerals. For example, if the value of the surface tension of the original emulsion was for a fresh surface and the value of the surface tension of the same emulsion after treatment with minerals was for an older surface, the difference may easily, and probably would, be a negative

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<sup>60</sup> *Loc. cit.*

<sup>61</sup> Taken by Taggart and Gaudin from *Min. & Sc. Pr.* (1921) 123, 232.

quantity. In no case have we found the surface tension of an oil-water emulsion to be lowered by treatment with mineral, if equilibrium surface-tension values only are used.

We have found, as shown by the above data, that the amount of oil removed from an oil-water emulsion by treatment with minerals is, in all cases, greater than a layer of oil on the mineral surface equivalent to one molecule deep. The oil removed by the minerals is equivalent to a layer 10 to 100 or more molecules deep. That the surface-tension method is indicating fairly closely the amount of oil removed from oil-water emulsions is shown by an independent method based on an entirely different theory.

#### FURTHER EXPERIMENTS ON MINERAL-OIL ADSORPTION AND COLLECTION BY MINERALS

Assuming that an equilibrium point exists between the amount of oil adsorbed at the water-solid (mineral) surface and that in the volume of the emulsion, we would expect adsorption of oil removed to increase with concentration up to the point of a complete layer of molecules or molecule aggregates, and to then show no further increase with concentration, unless the already heavily oiled mineral continued to collect on it more oil globules.

Surface tension-concentration curves *A*, *B*, *C*, and *D*, Fig. 18, for Burgess green camphor oil and the lower curves of Fig. 19 for Sunny South "C" pine oil before and after treatment with galena were constructed; 314 sq. cm. of galena surface (by calculation) were used in each test. From these curves, the adsorption\* concentration curves *E* and *F*, Fig. 18, were deduced.

Curves *A* and *B*, Fig. 18, are by the drop-weight method and curves *C* and *D* by the film method of measuring surface tension. The concentration-adsorption curves *E* and *F* as determined by the film and drop-weight methods, respectively, coincide exactly to a concentration of 20 mg. Curve *E* continues in a straight line to a concentration of 30 mg., while curve *F* shows adsorption past this point increasing more rapidly than concentration. It is significant that both methods give practically the same results for concentrations between 0 and 20 mg.

The film method, for this oil, is not applicable beyond 20 mg. per 100 c.c. water, as at this point the surface tension-concentration curves before and after treatment with mineral are nearly coincident, actually running together at 30 mg. The drop-weight method is more applicable to this oil (green camphor) than to any others tested, because of the great decrease in surface tension with very small quantities of oil and to the relatively high extent to which minerals collect it.

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\*The word "adsorption" is used in this connection for the want of one more fitting.

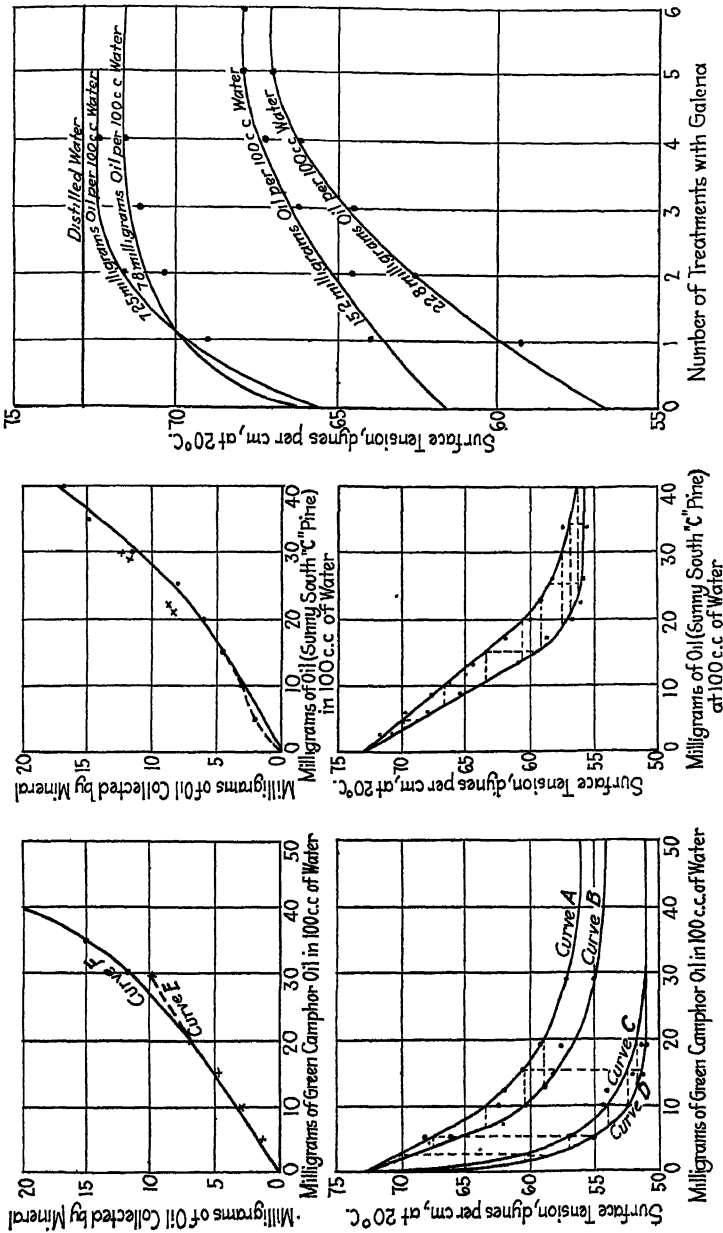


Fig. 20.

Fig. 19.

Fig. 18.

FIG. 18.—SURFACE TENSION-CONCENTRATION CURVES FOR GREEN CAMPHOR OIL, BY TWO METHODS OF MEASURING SURFACE TENSION, BEFORE AND AFTER TREATMENT WITH MINERAL, AND THE RESULTING CURVE SHOWING OIL COLLECTED BY MINERAL AT DIFFERENT OIL CONCENTRATIONS.

FIG. 19.—SURFACE TENSION-CONCENTRATION CURVES FOR PINE OIL IN WATER, BEFORE AND AFTER TREATMENT WITH MINERAL, AND CURVE PLOTTING OIL COLLECTED AGAINST CONCENTRATION OF OIL.

FIG. 20.—INCREASE IN SURFACE TENSION OF OIL EMULSION BY SUCCESSIVE TREATMENT WITH NEW BATCHES OF MINERAL.



From the adsorption-concentration curves, we are unable to find a point that indicates maximum adsorption of oil by the mineral. It was expected, as in the case of water-air surfaces, that a concentration would be reached when the adsorption-concentration curve would run parallel to the concentration ordinate. Adsorption appears to be practically a straight-line function of concentration over a range of 20 mg., beyond which the curves indicate adsorption increasing more rapidly than concentration. Any effort, however, to explain what is happening beyond a concentration of 20 mg. in 100 c.c. of water would be useless because the surface tension-concentration curves are of doubtful value beyond this point. Figures on adsorption of oil by minerals that are obtained from surface tension-concentration curves beyond the range of  $\frac{ds}{dc} = \text{a constant}$  are questionable.

Surface tension-concentration and adsorption-concentration curves for Florida Products Co. flotation oil "C," a pine oil, are given in Fig. 19. In general, the concentration-adsorption curve is similar to that of green camphor oil. It does, however, indicate more rapid adsorption between 0 and approximately 5 mg. per 100 c.c. than between the ranges 5 and approximately 15 mg., beyond which point it deflects rapidly from the general straight line toward the adsorption ordinate. A number of other oils give this same curve, some of them with even sharper turns.

Remarkably high percentages of the total oil in the emulsion are removed when treated with mineral particles. As much as 40 per cent. of the oil added, according to figures, is removed when the emulsion is treated with galena particles representing a total of 300 sq. cm. of surface.

For this same oil, we have data obtained by a method based on entirely different principles; namely, a nephelometric method\* which is based on turbidity of the emulsion. The data given in Table 32 were obtained by Ernest J. Baldwin, assistant professor of chemistry of the University of Idaho. The oil used was Florida Products oil "C" out of the same bottle of oil used in the surface-tension work and -28-mesh + 35-mesh galena out of the same lot prepared for the surface-tension work, was used. The calculated surface was 314 sq. cm.

The total number of milligrams of oil adsorbed on 314 sq. cm. of galena surface are plotted  $x$  on the curve Fig. 19, to facilitate direct comparison with the results as obtained by the surface-tension method.

Of the five points by the nephelometric method, represented by  $x$ , one point at 23 mg. falls on the curve plotted from surface-tension measurements, two points at approximately 30 mg. fall only slightly

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\* This method is extremely tedious and great care is required at all stages in the determination. Carefully purified ether was used as solvent for oil collected by the mineral particles. After the ether is distilled from the dissolved oil, the latter is taken up with alcohol and emulsified in a given amount of distilled water, the resulting emulsion being compared with standards of known concentration.

TABLE 32.—*Percentages of Oil Removed from Oil-water Emulsions Determined by the Nephelometric Method*

Volume, (Cu. Cm.	Weight of Oil, Milligrams	Milligrams Oil in 100 c.c. Water	Oil from Galena	Left in Emulsion	Per Cent. Adsorbed by Galena	Per Cent. Left	Per Cent. Re- covered
350	81.7	23.3	28.6	50.9	35.0	62.3	97.3
350	78.4	22.4	?	47.1	39.9	60.1 <sup>a</sup>	
350	76.4	21.8	?	47.8	37.5	62.5 <sup>a</sup>	
250	75.7	30.3	?	45.2	40.3	59.7 <sup>a</sup>	
250	74.3	29.7	29.0	43.9	39.0	59.1 <sup>a</sup>	98.1
250	99.8	39.9	53.5	44.03	53.6	44.1	97.6
250	101.5	40.6	54.5	?	53.6		

<sup>a</sup> By difference.

above the curve; while two more in the neighborhood of 22 mg. per 100 c. c. water are quite noticeable off the curve. The maximum difference in the adsorption, as obtained by the two methods, is approximately 10 per cent. The two methods indicate substantial agreement. It is unfortunate that no points by the nephelometric method are available farther down the curve, because the points plotted are actually above the most reliable range of the surface tension method.

Experiments in which emulsions of eucalyptus oil in water of different concentrations were repeatedly treated with fresh batches of galena particles gave the interesting data shown in Table 33 and in Fig. 20.

TABLE 33.—*Effect on Its Surface Tension of Successive Treatments of an Emulsion with Mineral*

Sample, Distilled Water	Surface Tension (20°)				
	Water 72.8	Emulsion No. 1 7.25 mg./100 c.c. H <sub>2</sub> O	Emulsion No. 2 7.8 mg./100 c.c. H <sub>2</sub> O	Emulsion No. 3 15.2 mg./100 c.c. H <sub>2</sub> O	Emulsion No. 4 22.8 mg./100 c.c. H <sub>2</sub> O
Emulsion.....		65.6	66.3	61.5	56.5
Emulsion plus galena.....		68.9	70.0	64.1	59.3
Emulsion plus galena, No. 2...		71.7	70.3	64.5	62.8
Emulsion plus galena, No. 3...		72.3	71.1	66.3	64.5
Emulsion plus galena, No. 4...		72.3	71.6	67.2	66.2
Emulsion plus galena, No. 5...		72.4	71.6	68.0	67.1
Emulsion plus galena, No. 6...			71.5	68.0	67.3

NOTE.—10 grams of -28-mesh + 35-mesh galena were used in each batch.

From the surface tension-concentration curve for eucalyptus oil, it is determined that these final surface-tension values represent concentrations

equivalent to roughly 1.0, 2.0, 6.5, and 7.4 mg. per 100 c.c. water, respectively. Emulsions No. 1 and No. 2 reach an apparent maximum surface tension after the third or fourth treatment with galena, while in the case of emulsions No. 3 and No. 4, the surface tension is increasing very slowly after five and six successive treatments with galena. These data are suggestive. When the concentration of the emulsion is 7.25 mg. oil per 100 c.c. water, 87 per cent. of the oil is readily removed by the galena particles while 13 per cent. of the oil seems to resist removal by the galena. When the concentration is 7.8 mg. oil per 100 c.c. water, 74 per cent. of the oil is readily removed by treatment with galena while 26 per cent. remains in the water. When the concentration is 22.8 mg. oil per 100 c.c. water, 70 per cent. of the oil is readily removed by treatment with galena while the other 30 per cent. seems to resist removal.

In view of the experiments of Taggart and Gaudin on the adsorption of completely soluble substances from water by minerals, which show that the adsorbed layer is in general one molecule deep, and of the experiments given in this paper, which show that in the case of flotation oil-water emulsions the oil layer taken up by minerals is many molecules deep, it is highly probable that the concentration, indicated by the apparent constant surface tension reached after a number of treatments with fresh batches of galena, represents that portion of the oil which is in true solution in the water. With the amount of mineral surface used (314 sq. cm.), there would be no noticeable increase in surface tension after the true solution concentration has been reached. A film of oil one molecule deep on 314 sq. cm. of surface would demand of the surface-tension instrument sufficient sensitiveness to show the result to the second decimal place. From the surface-tension values of the above emulsion for the first, second, and third treatments, it may be shown that the amount of oil removed by each batch of mineral particles is equivalent to layers on the mineral surfaces of many molecules deep.

If this hypothesis of what has happened in the experiments of Table 33 is correct, we have a scheme of determining approximately the amount of oil for a given concentration in emulsion and in true solution in water. In the quantities (about 0.25 lb. per ton) used in flotation, according to this scheme, eucalyptus oil is in true solution to the extent of only about 10 to 20 per cent., the other 80 to 90 per cent. being there as tiny droplets.

#### RELATIVE COLLECTIVE CAPACITY OF MINERALS IN EQUILIBRIUM WITH RESIDUAL EMULSION OF EQUAL CONCENTRATION

From a surface tension-concentration curve of emulsions before and after treatment with different minerals, the following adsorption data were obtained:

Concentration of residual emulsion	MILLIGRAMS OF PINE OIL ADSORBED ON 100 SQ. CM. OF SURFACE	
	11 mg./100 c.c.	10 mg./100 c.c.
Galena.....	1.30	1.07
Pyrite.....	1.30	1.07
Chalcopyrite.....	0.93	0.97
Sphalerite.....	0.90	0.87
Chalcocite.....	0.77	0.67
Siderite.....	0.57	0.60
Quartz.....	0.50	0.50

## EFFECT OF CHEMICALS ON ADSORPTION OF OILS BY MINERALS

The oil used in this experiment, Table 34, was a steam-distilled pine oil known as General Naval Stores, No. 5. The order of adsorption as indicated by increase in surface tension, with and without chemicals, is given.

TABLE 34.—*Effect of Chemicals on Adsorption of Oils by Minerals*

	Mg Oil in 100 c.c./ Solu- tion	Surface Tension before Treat- ment	Increase in Surface Tension Through Treatment with Minerals					
			Galena	Chalco- cite		Chalco- pyrite	Sphal- erite	Quartz
Distilled water.....		72.8						
Water-oil.....	18.4	59.9	1.4	0.9	1.4	0.8	0.8	0.5
Water + CuSO <sub>4</sub> .....	18.4	72.2						
Water + CuSO <sub>4</sub> + oil.	18.4	59.9	1.3	0.8	1.1	1.3	1.5	0.8
Water + Na <sub>2</sub> HPO <sub>4</sub> ..	18.4	71.7						
Water + Na <sub>2</sub> HPO <sub>4</sub> + oil	18.4	58.8	1.8	1.8	0.0	1.8	0.2	0.0
Water + Na <sub>2</sub> CO <sub>3</sub> .....		71.6						
Water + Na <sub>2</sub> CO <sub>3</sub> + oil	18.4	56.3	4.0	2.8	1.3	1.4	0.4	0.3
Water + K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .....	18.4	71.7						
Water + K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + oil		57.6	3.4	0.9	1.8	1.1	1.0	0.0
Water + H <sub>2</sub> SO <sub>4</sub> .....	18.4	72.0						
Water + H <sub>2</sub> SO <sub>4</sub> + oil.		56.5	3.3	2.3	2.1	2.1	1.6	0.0
Water + Na <sub>2</sub> S.....	18.4	71.2						
Water + Na <sub>2</sub> S + oil..		56.5	3.6	2.0	2.8	2.3	1.7	1.2
Water + NaOH.....	18.4	70.8						
Water + NaOH + oil.		55.6	2.2	0.8	0.8	1.3	0.0	0.0

NOTE.—Strength of solution, 0.087 per cent., which is equivalent to approximately 4 lb. per ton of ore in flotation.

Galena, in general, causes the greatest increase in surface tension of the emulsion. With copper sulfate in solution, the increase in the surface tension of the emulsion is greatest for chalcopyrite and sphalerite. With Na<sub>2</sub>HPO<sub>4</sub> and particularly Na<sub>2</sub>CO<sub>3</sub> in solution, the surface tension of the emulsion is markedly increased by galena and only slightly increased by sphalerite. The two reagents increase the flotation property of galena and decrease that of sphalerite. These facts are in favor of the idea

that the capacity of minerals to take up oil is in relation to, or a measure of, the flotability of the mineral under that condition. This, however, need not necessarily be true for it would seem that all that is necessary is a complete film of the oily substance around the mineral particle.

#### ADSORPTION, AGITATION AND TIME FACTORS

In the foregoing experiments, the time of agitation of mineral with emulsion was 2 min.; the following tests, Table 35, were designed to determine the rate of adsorption. Burgess green camphor oil was used and surface tension was measured by the film and drop-weight methods. The

TABLE 35.—*Effect of Time Factor and Agitation on Surface Tension of an Oil-water Emulsion*

Sample	Film Method	Increase in Surface Tension	Drop-weight Method	Increase in Surface Tension
Distilled water.....	72.8		72.8	
Emulsion, approx. 10 mg./100 c.c. water.....	51.6		62.6	
Emulsion, after 4 min. treatment with galena.	52.6	1.0	63.5	0.9
Emulsion, after 15 min. treatment with galena.....	53.3	1.7	64.5	2.0
Emulsion, after 30 min. treatment with galena.....	54.8	3.2	66.3	3.5
Emulsion, after 45 min. treatment with galena.....	55.3	3.7	66.7	3.9
Emulsion, after 60 min. treatment with galena.....	56.4	4.8	67.2	4.4
Emulsion, after 2 hr. treatment with galena..	56.5	4.9	68.0	6.0

figures indicate a slow rate of oil collection by minerals and, in view of the light of this experiment, previous so-called adsorption data should be considered as indicating the rate of mineral-oil removal rather than adsorptive capacity.

This experiment also has a significant bearing on agitation. The following flotation tests show that time of agitation, as well as kind of agitation, is of importance.

Time of Preliminary Agitation	Grams Concentrate	Grams Tails	Per Cent. Lead in Concentrate	Per Cent. Lead in Tails
4 min.....	27	123	41.0	1.9
15 min.....	30	120	38.5	1.3
30 min.....	27	123	43.7	0.7
1 hr.....	23	127	51.9	0.3

Adsorption tests with air and in the absence of air demonstrated that maximum adsorption is reached much more quickly when air is beaten into the pulp than when air is excluded. The explanation is, probably, that the minerals take on oil more readily when they are caused to pass through water-air (bubble surfaces) than when simply allowed to fall through the emulsion; there is an excess concentration of the oil on the water-bubble surface.

### SUMMARY AND CONCLUSIONS

1. This section is a consideration of the oil-collecting properties of the various common minerals met with in the flotation process. Emulsions of various common flotation oils and solutions of a variety of pure organic substances are treated with the various minerals. The amount of the substance in emulsion or in solution with the water is determined before and after treatment with the mineral by a surface-tension method. From a predetermined surface tension-concentration curve of the substance to be tested and from a knowledge of the total mineral surface, the amount of oil collected by the mineral per unit of area can be closely approximated.

2. The absolute correctness of the method is not established, but the evidence obtained seems well to support it. There is a fairly close agreement in results as obtained by two surface-tension methods and the nephelometric method. The method is rapid and gives concordant results, conditions being kept constant.

3. Assuming that an equal number of square centimeters of mineral surface was used in all tests, the data show that all minerals, including sulfides and gangue minerals, collect oil from oil-water emulsions; but that sulfides collect considerably more than gangue mineral; that the oil-collecting capacity of the sulfides is different for the same substance; that the order is different for various substances; and that galena invariably has the greatest oil-collective capacity.

4. Estimations place the thickness of the layer of oil collected on the surfaces of various minerals at between 10 and 100 molecules deep for low oil concentrations. The depth of the oil layer increases with increase in oil concentration, which may be explained by the theory that the oil is present in the water as molecule aggregates or tiny droplets and is collected by the minerals as such. As the droplets increase in size with concentration, the thickness of the oil layer also increases in depth.

5. Pure organic substances emulsified or dissolved in water are concentrated at mineral surfaces. No definite relation between molecular structure and degree to which substances are collected by the various minerals is established. Experiments were not carried far enough to draw any conclusion. Minerals possess decided selective collecting properties for pure substances in water as well as for oils.

6. Experiments in which a given emulsion is treated successively with new batches of mineral particles indicate: (a) that the surface tension of the emulsion is increased by each mineral treatment for a given number of treatments, when the surface tension reaches an apparent maximum; (b) that the apparent maximum surface tension is less the higher the original concentration of the oil emulsion; and (c) that the amount of oil collected by the mineral is less with each successive batch of mineral, ranging from the equivalent of oil layers many molecules deep to layers approaching a single molecule deep. In the case of the oils tested it would appear: (a) that before the apparent maximum surface tension of the emulsion is reached, the mineral particles are collecting oil droplets from a true oil-in-water emulsion; and (b) that after the apparent maximum surface tension is reached, we are dealing with a true solution and that oil molecules are being adsorbed by the mineral. The original emulsions are turbid while the final solutions are clear to the eye.

7. Chemicals profoundly affect the oil-collecting properties of minerals. The normal order of minerals in their oil-collecting capacity may be entirely upset by the presence of a small amount of an electrolyte in solution.

8. The drop-weight and the film methods of measuring surface tension give practically identical oil-collection concentration curves.

9. The maximum amount of oil that a mineral will remove from an oil-water emulsion is obtained more quickly when numerous air bubbles are beaten in with the mixture than when the minerals are simply allowed to fall through the emulsion.

#### ACKNOWLEDGMENTS

The research outlined in these papers was carried out in the laboratories of the School of Mines, University of Idaho, in cooperation with the Idaho Bureau of Mines and Geology.

The author wishes to express his appreciation of the many courtesies extended him by the University Departments of Chemistry, Physics, and Agriculture. He is indebted to Francis A. Thomson, Dean of the School of Mines and Secretary of the Idaho State Bureau of Mines and Geology, for appreciation of the purpose of the research and for his interest in it; to R. B. Elder, Assistant Professor of Metallurgy in the School of Mines, for his helpful suggestions from time to time; and to S. N. Shanfield, Ralph Jourdan, and Eugene Zanger, Fellows in Metallurgy, for their invaluable assistance in parts of the experimental work. The author also wishes to thank Oliver C. Ralston and Dr. L. D. Roberts, members of the Berkeley Station of the Federal Bureau of Mines, for their many comments and criticism of the work.

## DISCUSSION

ARTHUR F. TAGGART, New York City, N. Y.—The author states, on p. 735, that estimates “place the thickness of the layer of oil collected on the surfaces of various minerals at between 10 and 100 molecules deep for low oil concentrations.” Such thick layers are not to be expected from consideration of the molecular forces acting, and my experimental work leads rather to the conclusion that 90 to 99 per cent. of such quantities of oil is present on the mineral particles as droplets. Of course, if the total thus abstracted is averaged over the total surface, it corresponds to layers of the molecular thicknesses mentioned by the author. but in the present state of our knowledge it should not be thought to exist in the physical state of a uniform layer.

A. M. GAUDIN,\* Philadelphia, Pa. (written discussion).—The author presents the results of investigations that emphasize the molecular character of flotation phenomena. In this connection it might be interesting to describe a striking experiment devised by Dr. Irving Langmuir. A drop of nujol placed on the cleaned surface of a body of water fails to spread, but if a minute amount of oleic acid, pine oil, or amyl acetate is placed on top of the nujol drop by means of a looped platinum wire, within a short time the drop spreads vigorously. This indicates that the oil added to the nujol has diffused through the drop and reached the water. We infer that the surface tension of the contaminated nujol plus the interfacial tension between it and water is less than the surface tension of water, while the surface tension of nujol alone plus the interfacial tension between it and water is more than the surface tension of water. This result can be explained satisfactorily by postulating that the oleic acid, pine oil, or amyl acetate molecules orient themselves with their polar ends toward the water and their non-polar end toward the nujol, to decrease the nujol-water interfacial tension.

When such considerable effect as the spreading of a comparatively large oil drop is brought about by minute amounts of certain substances, the importance of contamination in surface-tension investigation is emphasized. Contamination might, for instance, account for some of the differences recorded by various observers for the surface tension of pure water, as tabulated on p. 653. Contamination of the character just related is likely to occur in the use of paraffined glass containers, as pointed out, on p. 675, in the sixth conclusion.

The evidence, in Table 4, as to the contamination of tap water can be profitably compared with a surface tension-contamination curve for

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\* Research Department, The Midvale Co.



oleic acid.<sup>62</sup> In drawing a curve, Fig. 21, from the results contained in Table 4, the abscissa chosen is "crowding" of the molecules of contaminant upon reduction of the contaminated surface to lesser and lesser areas. It is the exact counterpart of "amount of oleic acid added" at the other curve. The similarity between the two curves is such that one would easily mistake them one for the other, and points conclusively to a substance closely allied to oleic acid as the cause of the contamination, rather than to  $\text{CO}_2$ , as suggested by the author.

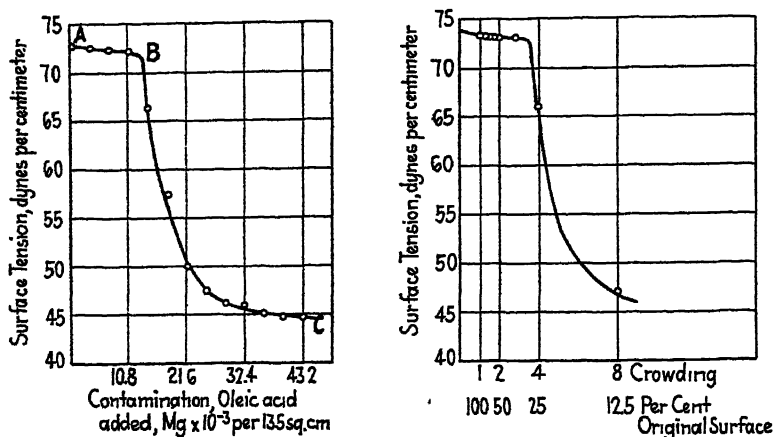


FIG. 21.

The time factor is emphasized in connection with the determination of surface tensions. It is unquestionable that a certain time is required to attain equilibrium between a freshly formed surface and the bulk of a liquid; but while a comparatively long time may be required for particles animated by Brownian movement, such as emulsion particles or for colloid particles, the time required should be much smaller for molecular or ionic solutions, the elements of which move at tremendously greater speeds. On reaching the surface, emulsion or colloidal globules probably lose their individuality to become part of a layer; while this is not true of molecules or ions, so that one may look on adsorption at the surface of an emulsion as being essentially a different process from that of adsorption at the surface of a true solution or at the interface between a true solution and another phase. While he criticizes surface-tension measurements of true solutions in which the time factor is disregarded, the author gives no evidence whatever to support his view that the surface tension of solutions diminishes with age. Such evidence, however, is necessary to compel a change in the accepted view that adsorption from a true solution is instantaneous, for all practical purposes.

<sup>62</sup> A. F. Taggart and A. M. Gaudin: Surface Tension and Adsorption Phenomena in Flotation. *Trans.* (1923) 68, 507.

During the process of adjustment leading to equilibrium between the surface and interior of an emulsion, a layer of oil gradually forms at the surface. It may never become visible by interference colors, as such colors appear only when the oil film reaches a thickness of the order of one-quarter of the wave lengths of light, *i. e.* from  $100 \times 10^{-7}$  to  $200 \times 10^{-7}$  cm.; in other words, the oil film would have to be of the order of 100 to say 400 molecules thick in order to become visible. Therefore the distinction which the author attempts to introduce, on p. 658, between the films formed by emulsions of higher and those of lower concentrations appears unacceptable, as it is a difference of degree rather than one of kind.

On p. 664, the author tabulates "the surface tensions of water on which films of a few common flotation oils have spread to their extreme limit and therefore are supposedly molecular" in which the value for oleic acid is given as 46.2. This value for oleic acid is generally accepted to be in the vicinity of 71.5 dynes per centimeter (Langmuir, Perrin, and others). On the other hand, when there is on the surface of water more than enough oleic acid to form a film one molecule thick, the surface tension is considerably lower than 71.5 dynes per centimeter. With three times as much acid as is necessary to form a monomolecular film, the surface tension was found<sup>63</sup> to be in the vicinity of 45 dynes per centimeter. This is in agreement with the figure of 46.2 dynes mentioned by the author. The sudden drop in surface tension from 71.5 dynes per centimeter, after oleic acid is added in excess of a monomolecular film, is understandable if one assumes that the oleic-acid molecules in excess of the monomolecular film are near enough to the water to have their OH<sup>-</sup> end oriented toward the water by the stray fields of the water molecules or ions (H<sup>+</sup> and OH<sup>-</sup>) and are crowding between the film molecules, thus causing a compression in the film great enough to reduce the surface tension so materially. Although there is no direct evidence to prove such a phenomenon, it gives a satisfactory picture of the mechanics of this "surface reaction."

The spreading coefficient given by the equation  $S = W_a - W_o$ , on p. 664, is applied by the author to complex mixtures, such as flotation oils. This should be done only with great caution for we have no evidence that it applies to systems other than true solutions composed of one solvent and one solute.

The author finds that the amount of oil removed by mineral particles from flotation oil-water emulsions would cover the mineral particles with a film from 10 to 100 molecules thick which he carefully and justly avoids calling an adsorbed film. In the footnote on p. 721 is suggested a very interesting and plausible explanation of the mechanism of adsorption from emulsions.

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<sup>63</sup> A. F. Taggart and A. M. Gaudin, *loc. cit.*

## Application of Sand-flotation Process to the Preparation of Bituminous Coal

BY T. M. CHANCE, PHILADELPHIA, PA.

(New York Meeting, February, 1924)

THE necessity of adopting improved methods of bituminous-coal cleaning at many collieries is recognized by all familiar with the requirements of the various bituminous markets, the approaching exhaustion of the relatively small areas of inherently high-grade coal, and the difficulties encountered in maintaining a uniform grade of shipped coal.

Many coals lose much of their market value by degradation in size, and, in any event, if the cleaning process is to contemplate wetting the coal the minimum amount of fines should be produced to prevent sludge losses and the difficulties resulting from the moisture content of the wet fines. Hence, it is desirable to bypass the finer coal dry, if this can be done without too great increase in impurities in the final product. This procedure has given excellent results at washeries at Steelton and in the Birmingham district. If the raw fines are too impure to permit admixture with the washed coal, it may be desirable to use dry methods, such as the pneumatic table, rather than to wet an excessive amount of such fine material.

The bituminous-coal cleaning plant should therefore: (1) Treat the raw coal in as large lump as possible and without sizing; (2) eliminate degradation of pure coal in the washing process; (3) avoid wetting the fines, if possible; (4) produce washed coal practically free from mechanically included impurities; (5) crush the refuse and retreat, if much intergrown coal and refuse are present, rather than precrush the entire feed.

Ordinary gravimetric methods of concentration, whether hydraulic or pneumatic, will not meet all of these requirements, as the large lump includes those sizes now sent to the picking tables, if it is desired to treat material of such size. I do not know of any prior commercial method, based on the falling velocity, coefficient of friction or resistance to fracture, that permits the production of clean coal varying in size from, say, 10-in. lump to  $\frac{1}{16}$ -in. mesh.

The effect on the specific gravity of any given coal as a result of variations in ash and pyritic sulfur content is well known; in fact, it has been made use of in commercially ascertaining ash content by deter-

mining the density of coal samples. Fig. 1<sup>1</sup> illustrates these relationships graphically. If a method of washing were used that made possible the production of washed coal at, say, 1.35 specific gravity, for the coal assumed in the chart, no piece of coal, whether 10-in. lump or  $\frac{1}{16}$ -in. mesh, of greater than 10 per cent. ash, and 0 per cent. pyrite sulfur, 6 per cent. ash and 0.5 per cent. sulfur, etc., would be included in the washed product. Such results would possess obvious inherent advantages.

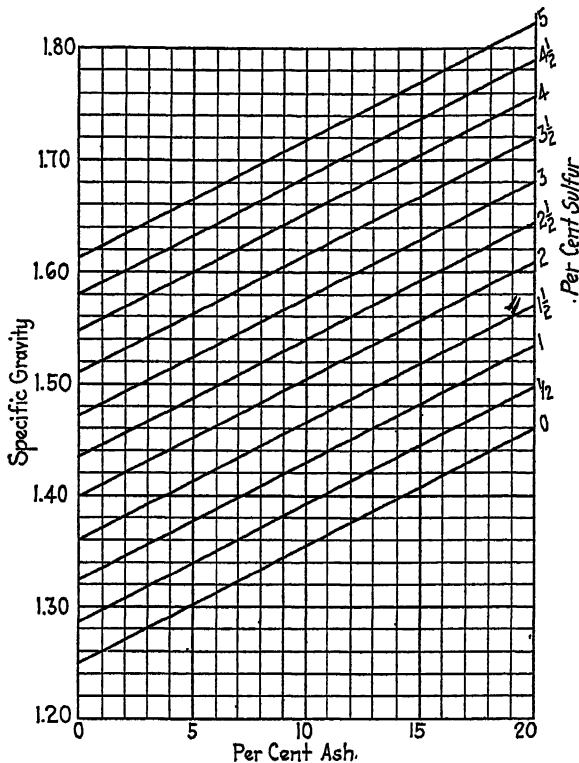


FIG. 1.—RELATION BETWEEN SPECIFIC GRAVITY OF COAL AND ITS PERCENTAGE OF ASH AND SULFUR, BASED ON FOLLOWING FACTORS: PURE COAL, SP. GR. = 1.25; CLAY ASH, SP. GR. = 2.3; SULFUR, 1 PER CENT. = 2 PER CENT.  $\text{FeS}_2$ , HAVING SP. GR. = 4.9.

The familiar float-and-sink test, using zinc chloride, or other, solutions, provides float and sink products dependent on these physical properties of the coal and refuse. On a laboratory scale, it makes possible a close approximation to separations based on the data of the curves in Fig. 1. The properties of the high-density solutions available for such flotational separations, however, are such as to preclude their

<sup>1</sup> A New Method of Separating Materials of Different Specific Gravities. *Trans.* (1918) 59, 267.

commercial use. There has been developed, however, what has been termed a fluid mass, of like characteristic as to density, of low viscosity that permits of its commercial use.

This method of separating materials of unlike specific gravity, using such a fluid mass is now known as the sand-flotation process.<sup>2</sup> The heavy density fluid mass is produced by maintaining a comminuted solid, such as sand, in suspension in a liquid, such as water, by the mechanical energy of agitating water introduced under pressure, a mechanical agitator, or a combination of both. The resultant process of separation makes possible the design of a coal-washery embodying the desirable features already enumerated.

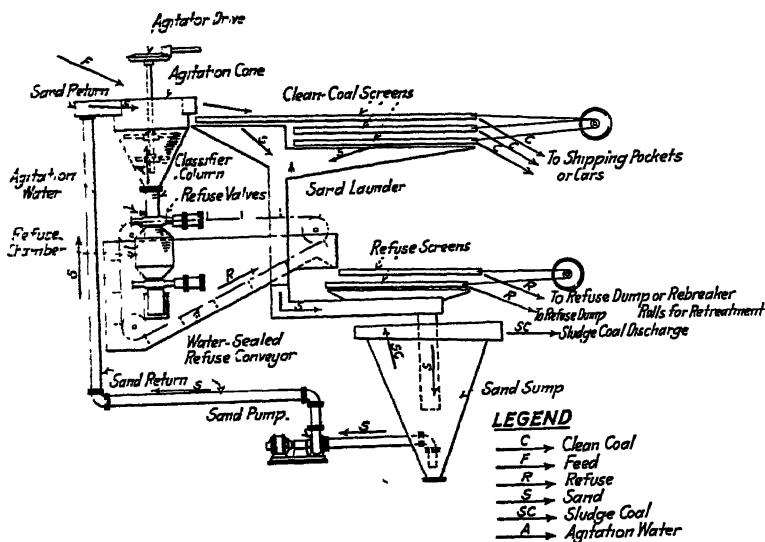


FIG. 2.—DIAGRAMMATIC ARRANGEMENT OF SAND-FLOTATION PROCESS FOR COAL.

Fig. 2 illustrates the elements of one form of apparatus commercially used in the washing of coal by this process. Many other types of equipment could be used, some of which are now being designed.

The fluid mass, an agitated mixture of sand and water, is contained in a cylindroconical receptacle provided with a cylindrical lower extension, called the classifier column. At the base of this column, slide valves and a refuse chamber are fitted for the removal of the refuse sinking in the fluid mass; the refuse thus trapped out of the cone passes into a water-sealed conveyor. Agitation is effected by water passing up the classifier column, assisted and distributed by slowly moving stirring arms. The water classifies out the greater part of the sand; the remainder is reclaimed on the refuse desanding screens.

<sup>2</sup> *Loc. cit.*

The raw coal is fed into the upper part of the cone; the refuse sinks and the coal floats in the upper part of the fluid mass. The floating coal is washed out of the overflow of the cone by the sand return from a centrifugal sand pump, the sand being reclaimed on the clean-coal desanding screens and, joining that from the refuse screens, passes to a conical sand sump connected to the sand pump.

This sand sump acts as a large classifier, the finer silt passing upward to the rim overflow with the agitator, shaker spray and other clear water and the coarser sand sinking to the sand-pump suction. The water overflowing the rim of the sand sump is passed to waste or to a sludge recovery tank for recirculation.

A layer of comparatively clear water is maintained on the top of the fluid mass in the separating cone. This has the dual function: it acts as a washing agent and assists in removing sand from the washed coal as it discharges upon the desanding screens, and it increases the relative buoyancy of the floating coal so that the coal rides higher in the top of the fluid mass.

Eight anthracite mining companies are now licensed to use the process; six plants have been placed in operation and three are under construction. Of these, six plants contain one 15 ft. diameter Type C separating unit, two plants contain two 7 ft. 8 in. diameter Type A units and one plant is provided with a single Type A unit. The 15 ft. Type C unit will treat up to 200 tons per hour of fresh-mined coal, or 150 tons per hour of culm (refuse) bank material. The 7 ft. 8 in. Type A unit will handle about 60 tons per hour of fresh-mined coal, or 30 tons of culm-bank material. In all the plants, an effort is made to remove the greater portion of the silt passing a  $\frac{3}{32}$ -in. hole screen before washing. At some of the plants, small silt screens (Hum-Mers or very high-speed shakers) are used for continuously screening silt from a bypassed part of the sand return. At the others, the sand return is pumped over the main desanding screens for a few minutes during the shift, after all the coal is out of the system; the shaker screens then act as sluices to riffle out the coal silt.

#### TYPES OF PLANT INSTALLED

The Lippincott Washery, of the Pine Hill Coal Co., has been chosen as a typical unit; its general arrangement is shown in Fig. 3.

This washery is laid out for a second 15 ft. unit to be located on the opposite side of the coal pockets, to handle fresh-mined coal; the combined fresh-mined coal capacity of the two units will be in excess of 2000 tons per day. The present plant is treating a refuse bank and fresh-mined coal from the Oak Hill breaker (located adjacent to the plant). Notwithstanding that all sizes from egg to barley are being washed in the one unit and that a high specific gravity is maintained to permit maximum bone extraction from the refuse-bank feed, the average of twelve cars of

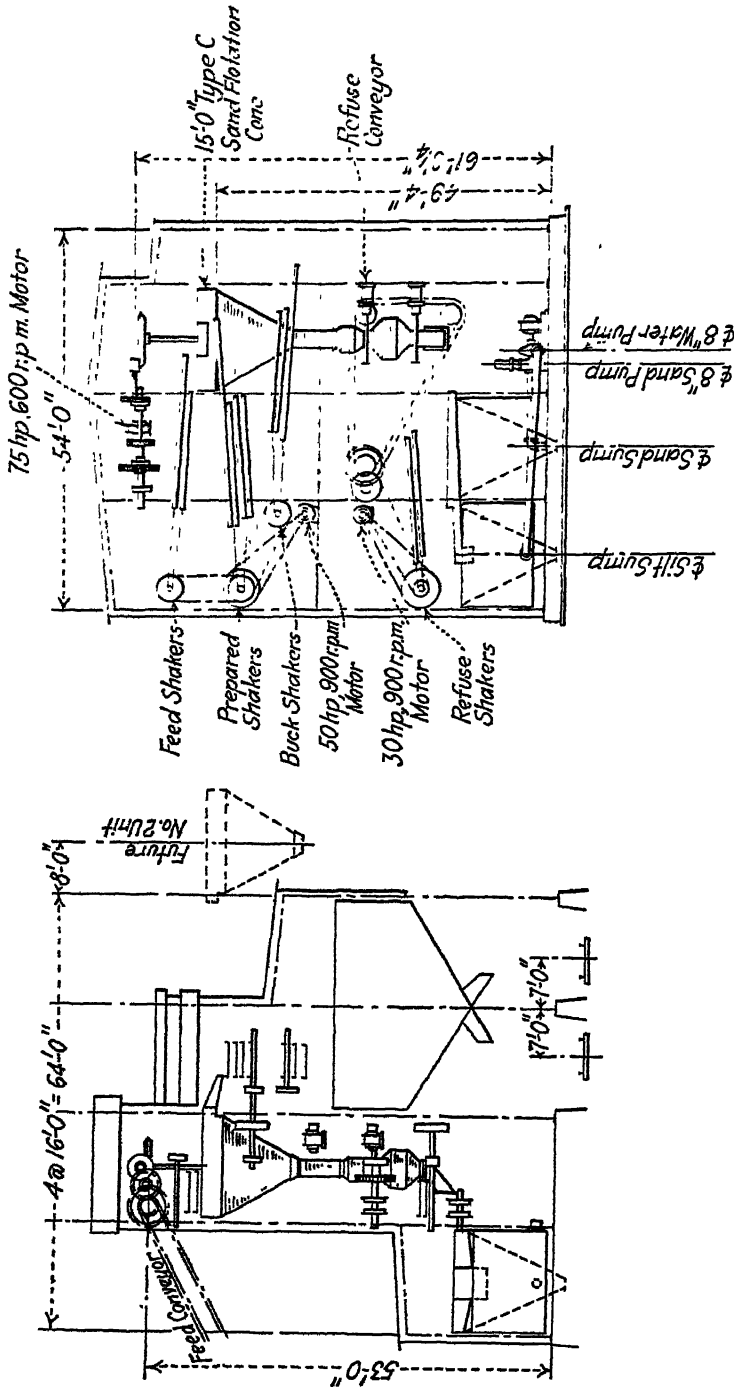


FIG. 3.—OAK HILL PLANT OF PINE HILL COAL CO. FOR CLEANING ANTHRACITE BY SAND-FLOTATION PROCESS.

No. 1 buckwheat produced during January, 1924, was but 10.9 per cent. ash.

Fig. 3 shows that the general layout is quite simple. The feed brought in by the intake conveyor passes over the feed shaking screens, which serve to remove the silt. The washed coal flows out of the cone and over the clean-coal shakers, which prepare the coal in seven sizes for market. The sand removed by the desanding elements of these shakers passes to the sand sump, to which is also returned the sand reclaimed from the refuse passing over the refuse shakers. This sand, which is used to produce the overflow of coal from the cone, is returned by the sand pump and piping system to the top of the cone. The comparatively clear water reclaimed from the sand sump passes to the adjoining silt sump, which serves as a settling tank, whence it overflows into the annular space between the conical lining and the cylindrical walls of the tank, which serves as the fresh-water sump. This fresh water is repumped into the main breaker system by a 1500-gal. centrifugal pump, and is thus continuously recirculated, over 80 per cent. being used for the shaker sprays and other miscellaneous supply of the system, and less than 20 per cent. being used for the operation of the main cone itself. The hydraulic cylinders on the slide valves are operated by a small clear-water hydraulic system served by a 3-in. centrifugal pump, so that nothing but perfectly clear water is ever used.

A portion of the sand return is passed over a Hum-Mer screen on its way to the sand sump; this screen removes part of the silt and thus prevents its accumulating to an objectionable amount. Of course, a certain amount of silt is removed continuously from the sand sump by the upward current of clear water, which flows from that sump to the silt sump, but enough coarse silt remains in the system to make some extraneous means of removing it from the sand desirable.

### OPERATING RESULTS

The close regulation that sand flotation provides is shown by the accompanying test results:

#### WILKES-BARRE DISTRICT; CHAUNCEY BREAKER; DENSITY 1.70

*Refuse to bank; average of all sizes. Visual inspection; daily averages*

1923	COAL, PER CENT.	BONE, PER CENT.
June 7.....	0.73	2.30
June 8.....	2.43	6.25
June 9.....	0.22	1.67
June 11.....	0.11	1.15
June 12.....	0.84	3.50
June 13.....	0.84	3.60
Average.....	0.84	3.08



# 746 SAND-FLOTATION PROCESS FOR PREPARATION OF BITUMINOUS COAL

## AVERAGE OF COAL SHIPPED, WEEK JUNE 11, 1923

	SLATE, PER CENT	BONE, PER CENT
Egg.....	1.9	4.6
Stove.....	2.5	3.8
Nut.....	2.6	2.3
Pea.....	4.0	
Buckwheat.....	2.5	

## HAZLETON DISTRICT, BEAVER BROOK BREAKER; DENSITY IN CONE 1.75

*Refuse leaving cone before crushing and rewashing; inspection by zinc chloride, float and sink at 1.75 sp. gr., daily average*

1924	STOVE AND LARGER FLOAT, PER CENT.	NUT AND SMALLER FLOAT, PER CENT.
Jan. 30.....	1.25	3.17
Jan. 31.....	1.60	1.50
Feb. 1.....	4.50	3.80
Feb. 2.....	1.00	2.50
Average.....	2.09	2.74

Average coal by visual inspection, 1.83 per cent. all sizes.

Average bone by visual inspection, 10.96 per cent. all sizes (concentration due to recirculation).

## SCHUYLKILL DISTRICT, LIPPINCOTT (OAK HILL) WASHERY; 1.75 DENSITY

### *Washing Refuse Bank*

Average refuse, visual inspection.....	1.30 per cent. coal	3.4 per cent. bone
Washed egg, visual inspection....	1.25 per cent. slate	1.0 per cent. bone
Washed stove, visual inspection.....	2.00 per cent. slate	2.0 per cent. bone
Washed nut, visual inspection.....	2.00 per cent. slate	
Washed pea, visual inspection.....	2.50 per cent. slate	
Washed buckwheat (including fresh-mined).....		10.9 per cent. ash

## MAINTENANCE

Some concern has been shown as to maintenance costs because of the introduction of sand flotation. Table 1 gives the average length of life, material costs, and cost per ton, based on the operating results of the past two years. Monthly shipments of 25,000 tons from a single 15 ft. Type C machine, fitted with an 8-in. sand pump are assumed. The figures are the maximum prices paid for the various items; some of the licensees have materially lowered their unit costs; also material, such as screen segments, that should be partly charged to supplies is included. These items cover all those that can be directly charged to sand flotation; against them should be balanced jig and table upkeep, together with a portion of the screen equipment of the ordinary breaker, together with a considerable credit as a result of the much lower maintenance on the smaller, more compact building and drives necessary. The maintenance costs given

are total cost delivered at the colliery. They do not include labor, as colliery renewals of this kind are generally handled by a repair crew that is constantly employed on general breaker upkeep.

TABLE 1.—Maintenance Costs

	Cost	Life, Months	Tonnage	Per Ton
Complete sand-pump manganeese-steel renewals.....	\$480.00	3	75,000	\$0.0064
Refuse conveyor chain.....	320.00	6	150,000	0.0021
Refuse conveyor flights.....	190.00	9	225,000	0.0009
Desanding screen segments .	270.00	2	50,000	0.0054
Slide valves .....	400.00	6	150,000	0.0027
Slide-valve chests.....	490.00	12	300,000	0.0016
Total maintenance per ton....				<u>\$ .00191</u>

## BITUMINOUS COAL WASHING

Three typical flow sheets that may be used to meet various soft coal operating conditions are shown in Fig. 4. Flow sheet No. 1 illustrates the simplest case, in which the feed contains but little refuse intergrown with coal, bone, or pyrite. No. 2 is a more complicated arrangement, refuse

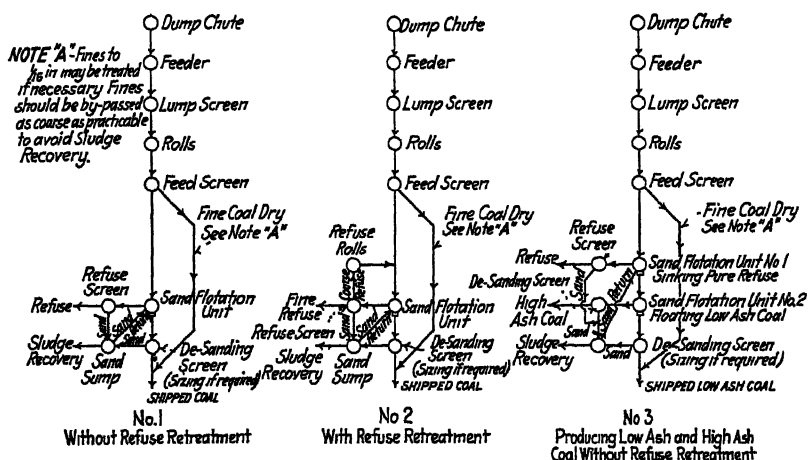


FIG. 4.—TYPICAL FLOW SHEETS FOR CLEANING BITUMINOUS COAL BY SAND-FLOTATION PROCESS.

crushing and retreatment being desirable because of the presence of considerable such intergrown material. No. 3 represents the case in which large amounts of bone, or high-ash coal, make desirable a two-part separation. Refuse crushing and retreatment is not shown but may be employed if much intergrown material is present, the crushed refuse being returned to the original feed.

These flow sheets are purely diagrammatic and, of course, are subject to a variety of combinations. The  $\frac{3}{16}$ -in. fines should be kept dry, if at all possible, because sand flotation produces little sludge; hence if the raw fines are dry, much of the difficulty experienced with wet fine coal is eliminated. However, if it is impossible to bypass the fines in the raw state, or after dry cleaning, we would wash everything down to  $\frac{1}{16}$ -in. mesh, as sand flotation will produce the same ash and sulfur reductions in these fines sizes as in the large sizes. The only objection to including them is the wetting of any fine coal unless absolutely necessary.

### BITUMINOUS WASHERY ESTIMATES

The estimates of construction, operating, and capital cost for a bituminous washery, designed to ship 1000 tons per day, are as follows. This washery has been laid out to utilize flow sheet No. 2, for the preparation of coking coal; but one shipping track is, therefore, required and the expense of pockets or multiple loading tracks is obviated. The estimates include the necessary equipment for silt recovery.

#### CONSTRUCTION COST ESTIMATE

Foundations, 150 yd. @ \$22.....	\$ 3,300.00
Steel frame, 165,000 lb. @ \$0.07 erected.....	11,550.00
Siding, 100 sq. @ \$35 including glazing .....	3,850.00
Roofing.....	400.00
Roof, floors, tanks, pockets, and all other timber construction, 37,000 ft. @ \$120.....	4,440.00
Rotary dump.....	3,500.00
Feeder.....	500.00
Washery machinery, including 36 by 34 in. rolls, 24 by 30 in. rolls, shafting pulleys, gearing, belting, shaker screens, etc.....	12,842.00
Intake conveyor, 30-in. rubber belt, idlers and pulleys.....	1,400.00
Type B coal washer, slide valves, and thrust cylinders.....	5,000.00
Type B sand sump.....	1,200.00
8-in. direct-connected sand pump, manganese-steel lined.....	1,100.00
10-in. direct-connected water pump.....	600.00
3-in. direct-connected slide-valve pump.....	200.00
Piping.....	2,500.00
Silt sump and conveyor.....	2,300.00
Motors and wiring.....	5,300.00
Machinery erection.....	4,000.00
	<hr/>
	\$63,982.00
10 per cent. for contingencies.....	6,398.20
	<hr/>
	\$70,390.20

Heating, lighting, substation transformers, mine-car trestles, railroad siding, and refuse disposal not included.

## OPERATING COST AND CAPITAL COST ESTIMATE

The following estimates of operating and capital cost are based on operation with a force account as below:

Foreman.....	1			
Car dumpers. . . . .	2			
Oilers.....	2			
Cone runner.....	1			
Slate valves.....	1			
Pump runner.....	1			
Railroad car loaders.....	2			
Silt recovery.....	1			
Refuse disposal.....	1			
<hr/>				
Total.....	11 men	@ \$7	\$77	
	1 Foreman	@ 10 =	10	
				<hr/>
				\$87

## OPERATING AND CAPITAL COST 1000 TONS WASHED COAL PER SHIFT

	PER TON WASHED COAL
Labor, 12 men, \$87.....	\$0.087
Power, 295 hp. connected-load @ 75 per cent., 1770 kw.-hr. @ \$0.02...	0.036
Sand, 1 per cent. loss at \$4 per ton.....	0.040
Oil and supplies.....	0.020
Maintenance.....	0.020
Fixed charges @ 12 per cent. on \$70,000 plant cost, @ 280,000 tons per annum.....	0.030
<hr/>	
Total operating and capital cost .....	\$0.233

## Production of High-grade Blast-furnace Coke

By H. M. CHANCE, PHILADELPHIA, PA.

(New York Meeting, February, 1924)

RECENT research work has shown that coal can be produced, at reasonable cost, from almost all coal-mining districts containing not more than 3 to 8 per cent. of ash. From coal so produced, an abundant supply of coke, suitable for blast-furnace operation, can be made containing from 12 down to 6 per cent. or less of ash.

These statements apply broadly to the Appalachian coal belt, including most of the mining districts in Pennsylvania, Ohio, West Virginia, Kentucky, Tennessee, and Alabama. The exceptions will generally be found among those coals carrying a prohibitive percentage of sulfur. Any gravimetric heavy fluid method of separation will effect a reduction in the percentage of sulfur, but this reduction may not be sufficient to produce, from coal unfit for metallurgic use, a product that can be so used. When a large part of the sulfur is in the form known as "organic sulfur," or is present as very finely disseminated and homogeneously distributed pyrite, possibly it cannot be eliminated from the low-ash coal produced. When the sulfur exists as pyrite in distinct layers, bands, or nodules, or when it is finely disseminated but is irregularly distributed, often a low-ash coal low enough in sulfur to make good metallurgic coke can be produced from relatively impure coals.

It has generally been assumed that the quality of coke on which blast furnaces must be operated depends on the geographic location of the furnace, and that the grade of coke on which a blast furnace must operate is that produced from the best coal obtainable by careful mining; or if the coal is prepared by washing, hand picking, or other means by which the foreign impurities are removed, that the grade of coke on which the furnace must operate depends on what has been termed the "inherent ash" of the particular coal.

The term "inherent ash" is generally understood to mean the percentage of ash present after all removable (free) impurities, slate, fireclay, high-ash bony coal, and pyrite have been removed, and is usually applied to the percentage of ash present in run-of-mine coal from any mine after these impurities have been removed. Perfect washing, or perfect preparation, is understood to be attained when the percentage of ash in the washed coal is reduced to the percentage of inherent ash; that is, of ash that cannot be removed by the washing processes in common use. Wash-

ing plants operated with this end in view generally can produce a product approximating the percentage of inherent ash by crushing most of the coal to small size.

It is, of course, well known that the inherent ash in different benches or layers of coal may vary widely; in some benches it may be 6 per cent. in others 10 or 12 per cent. and in others still higher. This condition has brought about selective mining in which impure benches of coal in the upper or lower part of a coal bed are not mined, being left in place untouched; if in the middle part of the coal bed, they are separated from the rest of the bed by the miner, or, by the system of mining used, are separately mined and thrown aside as refuse.

Many observers have commented upon the concentration of the ash in planes parallel to the stratification of the coal, producing layers or laminæ of high-ash coal alternating with layers or laminæ of low-ash coal,<sup>f</sup> these being quite evident even on casual examination. It has, however, been generally assumed that when a coal bench, say 4, 6, 10 in. or more thick, contains no visible stratified layers but is characterized by cleavage approximately at right angles to the bedding, developing what is known as the "finger" or "columnar" structure so that the coal of such bench or layer naturally breaks into long slender columns, the inherent ash is uniformly distributed; that is, if the coal of such a bench shows by analysis, for example, 6 per cent. of ash, individual lumps or pieces into which the coal may be broken will each contain practically the same percentage of ash. The research work on which the foregoing conclusions are based has shown that uniform distribution of the inherent ash in any bench or portion of a coal bed is the exception and not the rule; that a bench of coal, such as that just described, showing 6 per cent. of ash may often consist of an irregular admixture of coal ranging from 2 up to 12 or 15 per cent. of ash. If the pieces into which such coal are broken are separately analyzed these large variations in ash will be disclosed. In other words, the distribution of the inherent ash in coal is extremely irregular, because coal is not a homogeneous mixture of low-ash and high-ash coal.

This generalization applies practically to all coals. Coals in which the inherent ash is high, say 10 per cent., may often consist of an admixture of coal ranging from 2 to 20 per cent. ash; to produce from such a coal a phenomenally low-ash product, it is therefore only necessary to separate the low-ash coal from that of higher ash content.

The method suggested consists in first removing the separable impurities, slate, rock, fireclay, pyrite, etc., and in then making a differential separation of the coal into two or more products of relatively low and higher ash content. This differential separation generally need not be carried far enough to render the higher ash product worthless. For example, assuming the inherent ash in a given coal is 10 per cent. If the coal is divided into two equal parts, the low-ash half carrying 5 per cent. ash,

the higher ash half will contain 15 per cent. ash, which will largely reduce its value as a steam coal; but if 40 per cent. of the coal is separated as a 7-per cent. ash coking-coal product, the 60 per cent. of higher ash product will contain 12 per cent. ash and can be utilized as a fair grade steam coal; or 30 per cent. of 6-per cent. ash coking coal can be separated leaving 70 per cent. to be utilized as steam fuel containing 11.72 per cent. ash. If the inherent ash in a coal is 8 per cent., 50 per cent. may be separated as a 5-per cent. ash coking coal, leaving 50 per cent. as a steam coal with 11 per cent. ash.

Differential separations of this kind can often be carried out without fine crushing. A recent test of a run-of-mine sample of coal from the Pittsburgh bed in Westmoreland County, Pa., was made as follows: The coal showed by analysis 11.34 per cent. ash. The lumps were first broken so that all of the coal passed through a 4-in. round-hole screen. A screen analysis showed

	PER CENT.
Through 4-in. over $\frac{3}{16}$ -in. round-hole screen.....	48.07
Through $\frac{3}{8}$ -in. over $\frac{3}{16}$ -in. round-hole screen .....	33.14
Through $\frac{3}{16}$ -in. round-hole screen.....	18.79
	<hr/> 100.00

The 18.79 per cent. coal passing through  $\frac{3}{16}$ -in. screen was not washed, it showed by analysis 8.10 per cent. ash.

All the coal from the 4-in. size down to the  $\frac{3}{16}$ -in. was then separated from its removable impurities by float-and-sink method at a specific gravity of 1.29 and the refuse sinking at this gravity was separated by float-and-sink method at a specific gravity of 1.425 with the following result:

	PERCENTAGE	ASH
Coal floated at 1.29 sp. gr.....	37.77	4.75
Coal floated at 1.425 sp. gr.....	36.03	13.22
Refuse sunk at 1.425 sp. gr.....	7.41	44.00
	<hr/> 81.21	
Fines, through $\frac{3}{16}$ -in. mesh not washed.....	18.79	8.10
	<hr/> 100.00	<hr/> 11.34

The same coal separated at a specific gravity of 1.34 gave the following results:

	PERCENTAGE	ASH
Coal, floated at 1.34 sp. gr.....	48.68	5.50
Coal, floated at 1.425 sp. gr.....	25.12	15.44
Refuse, sunk at 1.425 sp. gr.....	7.41	44.00
	<hr/> 81.21	
Fines, through $\frac{3}{16}$ -in. mesh, not washed.....	18.79	8.10
	<hr/> 100.00	<hr/> 11.34

It is evident that the 18.79 per cent. of unwashed fines carrying 8.10 per cent. ash can be added to either the low-ash or the high-ash coal, so that by the two separations made coking coals and steam coals of the following weights and ash percentages can be produced. It will of course be understood that the percentage of low-ash coal recovered, and the percentage of ash, can be changed by increasing or decreasing the specific gravities at which the separation is made.

Pittsburgh Coal Westmoreland County, Pa.	Specific Gravity, 1.29-1.425				Specific Gravity, 1.34-1.425			
	Fines Added to Steam Coal		Fines Added to Coking Coal		Fines Added to Steam Coal		Fines Added to Coking Coal	
	Per Cent.	Ash	Per Cent.	Ash	Per Cent.	Ash	Per Cent.	Ash
Coking coal.....	37.77	4.75	56.56	5.87	48.68	5.50	67.47	6.22
Steam coal.....	54.82	11.46	36.03	13.22	43.91	12.30	25.12	15.44
Refuse.....	7.41	44.00	7.41	44.00	7.41	44.00	7.41	44.00
	100.00	11.34	100.00	11.34	100.00	11.34	100.00	11.34

Separations made on a sample of an Alabama coking coal carrying 8.98 per cent. of ash at specific gravities of  $1.25\frac{3}{4}$ , 1.29, and 1.37, the removal of refuse being in each case made at a specific gravity of 1.59, gave the following results:

Alabama Coking Coal	Specific Gravity, $1.25\frac{3}{4}$ -1.59		Specific Gravity, 1.29-1.59		Specific Gravity, 1.37-1.59	
	Per Cent.	Ash	Per Cent.	Ash	Per Cent.	Ash
Coking coal.....	34.61	1.86	75.48	2.52	87.92	3.50
Steam coal.....	58.33	5.91	17.46	12.55	5.02	20.19
Refuse.....	7.06	69.17	7.06	69.17	7.06	69.17
	100.00	8.98	100.00	8.98	100.00	8.98

It might be possible to lower the ash in the 5.02 per cent. of steam coal obtained in the separation made at 1.37-1.59 by recrushing such product and rewashing at the same or at a different specific gravity, but this will not be possible if this high-ash material consists principally of high-ash bony coal in which the ash is uniformly distributed. It will, of course, be understood that when any considerable quantity of high-ash bony coal of this description, that is with uniformly distributed ash, is present in a coal, its high ash must be obscured by adding to it considerable of the



lower ash coal to obtain a coal carrying such moderate percentage of ash as will permit of its use or sale as a steam fuel.

The described data are illustrated graphically in Fig. 1. Fig. 2 is an x-ray photograph, natural size, of a piece of Pittsburgh bed, coking coal, ground flat on both sides and  $\frac{1}{4}$  in. thick. It was exposed at a distance of 18 in. from the x-ray generator for 3 sec. The percentage of ash in this sample is probably not over 8 per cent. that being the average ash content of other pieces of coal of the same character forming a part of the same sample. It consists of irregular layers and laminæ of very pure coal interleaved with irregular layers and laminæ of relatively high-ash coal. The very pure coal is almost completely transparent to the x-rays, but

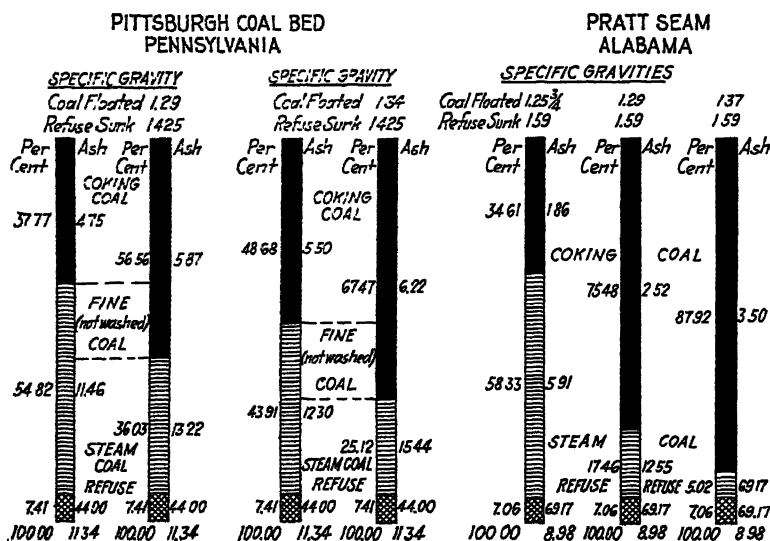


FIG. 1.—DIFFERENTIAL SEPARATION OF COKING COAL.

the materials comprising the ash are not transparent, so that the x-ray photograph shows the pure coal almost black and the high-ash coal of a lighter color, gray to white. Using the x-ray photograph as a negative, the photograph is obtained in which the pure coal is of a gray color the presence of higher ash being shown as darker gray, approaching black. By using thinner sheets of coal, we hope to obtain photographs that will show even more clearly the irregularity in the distribution of ash and the very common presence of high-ash and low-ash coal in close proximity to each other. It is not, of course, proposed to attempt differential separation on parts of coal beds exhibiting the very thin layers of low-ash coal shown by the photograph, because very fine crushing would be necessary to separate coal of the low-ash layers from that of higher ash. This particular specimen was selected to show how, even in a piece of coal

of apparently good quality there is the same irregularity in the distribution of the ash as is found in coal of inferior grades.

The operator of blast furnaces is confronted with the increasing scarcity of low-ash, low-sulfur coal suitable for making the best grades of metallurgic coke, with such increase in the demand for such coke as must accompany increase in the annual production of iron and steel products, and with increased or increasing impurities in formerly high-grade coal as now shipped from the mines. This deterioration in quality is more or less marked in nearly all mining districts, so that coals which as shipped in 1914 may have carried 6 to 10 per cent. of ash may now (1924) carry 8

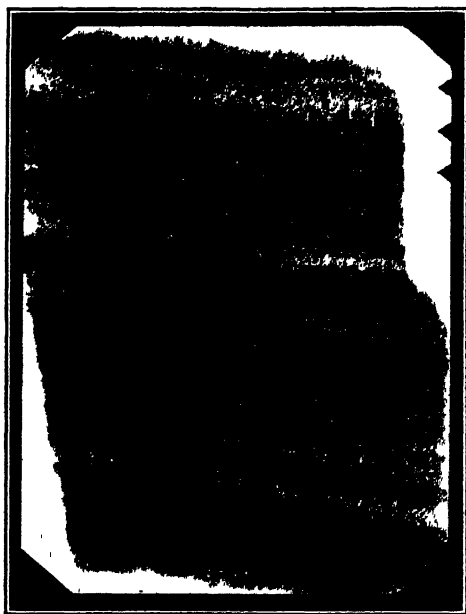


FIG. 2.—X-RAY PHOTOGRAPH SHOWING DISTRIBUTION OF ASH IN PITTSBURGH COKING COAL  $\frac{1}{4}$  IN. THICK. LIGHT-COLORED LAYERS ARE PURE COAL; DARK-COLORED LAYERS, IMPURITIES.

to 14 per cent. of ash, the increase in ash being generally due to the presence of free slate, shale, rock, or fireclay. This means that many coals that formerly could be used raw for making coke of good to fair grade, now must be washed unless the blast-furnace manager can successfully use cokes of poorer grade.

To meet the increasing tonnage required for making metallurgic coke, in the absence of sufficient tonnage of high-grade low-ash coal, it has been necessary in many cases to add to the high-grade coal available a quantity of coals of poorer grade, thus obtaining a mixture of two or more coals that will produce a sufficient quantity of coke, but of a grade inferior to

that available if high-grade coal alone is used, and much poorer than that available when the higher grade coals contained, as mined, a smaller percentage of impurities.

If coal is to be washed, or must be washed, the obvious plan is one providing not only for the elimination of free impurities but for the differential separation of the coal into at least two grades, because this differential separation can be effected at very small additional cost and will furnish the blast-furnace manager with coke superior to any heretofore attainable.

Differential separation, as herein outlined, makes available vast stores of low-ash coal locked up in coal beds from which it has been impossible to ship anything better than fair grades of steam coal.

Differential separations, such as those illustrated by the examples given, can be made by any liquid or solution having a specific gravity greater than that of the coal which is to be floated and less than that of the coal that is to be separated by sinking in the liquid. No liquids or solutions suitable for making such separations on a commercial scale have as yet been discovered or artificially produced. The nearest approach to such liquid or solution is a mechanical mixture of sand and water in which the sand is kept suspended in the water by mechanical or hydraulic agitation or by a combination of mechanical and hydraulic agitation which has come to be known as the "sand flotation process."

This process has already been described.<sup>1</sup> It is rapidly coming into use in the preparation of coal for market in the anthracite fields, where six plants are in operation, three are nearly finished, and others are being designed. The six operating plants have an aggregate capacity of over 1,000,000 tons annually and represent capital expenditures of about \$1,000,000. The first commercial installation was completed in the fall of 1921 and has been operating continuously (except during the suspension of work in the anthracite regions) for about two and a half years, giving the benefit of prolonged experience with the process when operating under varying conditions. This experience in the operation of machines using the process on a large commercial scale has developed the following certain characteristics of the process, which are of great importance in the washing of bituminous coal:

1. Separation can be made without the fine crushing required when washing coal by other methods.
2. Effective and satisfactory separation can always be made of unsized coal. Sizing by screening is unnecessary, one machine will take all sizes mixed.

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<sup>1</sup> Thomas M. Chance: A New Method of Separating Materials of Different Specific Gravities. *Trans.* (1918) 59, 263; also, Application of Sand-flotation Process to the Preparation of Bituminous Coal. See page 740.

3. The capacity is large; the maximum capacity is unknown. One machine 15 ft. in diameter has continuously been fed with unsized coal at a rate of over 200 tons per hour, with not more than 50 per cent. of the superficial area of the machine being actually used in effecting the separation. This would indicate a separating capacity of 2 tons or more per hour for each square foot of separating area.

4. The specific gravity of the separating medium (mixture of sand and water) can be closely regulated at any desired density and held approximately constant at the desired density.

5. The consumption of sand can consistently be kept at less than 1 per cent. by weight of the tonnage of coal treated and, with care in installation and operation, can be reduced to a small fraction of 1 per cent.

6. The production of sludge by attrition in the machine is extremely small.

7. When making a differential three part separation, the products are low-ash coal, containing practically no pieces of high-ash coal; high-ash coal, containing practically no pieces of low-ash coal or of refuse; refuse, containing practically no pieces of high-ash or low-ash coal.

While this paper has been prepared to present to the iron and steel industries the possibility of securing better coking coal and of obtaining coking coal from coal fields heretofore considered outside the pale from a coking standpoint, its application to the washing of bituminous coal is also adapted to the better and cheaper preparation of bituminous coals for steam, domestic, and other uses.

## Dry Cleaning of Coal

By RAY W. ARMS,\* E. M., CHICAGO, ILL.

(New York Meeting, February, 1924)

DRY CLEANING, or pneumatic separation, is not, strictly speaking, a recent discovery. Among the archives of the Patent Office may be found many patents dating back as far as 1850 which cover early attempts to separate materials of varying specific gravity or of different shape by means of air. Hundreds of patents covering this art have been issued, which may be roughly classified into four general groups, as follows:

1. Stationary devices with pulsating air currents. The separating surface is usually riffled and air is supplied by bellows or compressors. This group also includes air jigs, which have been used rather extensively.

2. Stationary devices with continuous air currents. These submitted the material to a continuous current of air, either horizontal or vertical. Chaff is blown from wheat by such a device.

3. Reciprocating or vibrating devices with pulsating air. A small group in which the pulsating air is supplied by bellows and some motion provided in the separating surface to move the stratified material to various discharge points.

4. Reciprocating or vibrating devices with continuous air supply. This is by far the most important group and all recent developments have been along this line.

All of the above groups involve the stratification of material by air and include none of the dry methods that use other principles, such as coefficient of friction, magnetism, etc.

### AIR STRATIFICATION

In all of the above groups of air separating devices, the same phenomena are found as exist in water concentrators; that is, free settling will be found in some and hindered settling in others, with a complex action on the reciprocating tables similar to the wet tables.

The experimental value of the settling ratios of particles in air has never been determined but, following the formulas given in Richards'

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\* Contracting Engineer, Roberts & Schaefer Co.

"Ore Dressing," they can be calculated. The formula for the settling velocity of particles in any medium is as follows:

$$V = C\sqrt{(\delta - \delta_1)D}$$

in which

$V$  = velocity of the particle

$\delta$  = density of the particle

$\delta_1$  = density of the medium

$D$  = diameter of the particle

$C$  = a constant depending on the shape of the particle and the units used.

The constants referred to have never been determined for coal and slate, but in the estimation of the writer the constant for slate will be about 0.85 of that for coal because of the usual tabular formation of the slate.

To determine the free settling ratio, which is the relation between diameters of particles settling in a medium at the same rate, the two velocities are equated and the ratio of the diameters determined. Thus:

$$100\sqrt{D_c (1.3 - 0.00124)} = 85\sqrt{D_s (2.6 - 0.00124)}$$

$$\frac{D_c}{D_s} = \text{free settling ratio of coal and slate in air} = 1.4$$

In wet concentration, it is a known fact that the hindered settling ratio is much larger than the free settling ratio and it is reasonable to suppose that the same holds true with air separation. From experiments that have been made so far, it is reasonable to assume that the hindered settling ratio is approximately 2.5. This settling ratio governs the sizing that must precede concentration and will vary in different coals.

#### QUANTITY AND PRESSURE OF AIR

The theoretical calculation of the amount of air that will be required to suspend a bed of coal and refuse sufficient to cause stratification is indeterminate, owing to the fact that this suspension is accomplished partly by the static pressure and partly by the velocity of the air; but the two limits caused by these factors may be found, and the calculation is determinate to that extent. The effects of these two factors may be observed best by considering the extreme cases: first, of a single particle of coal being lifted or suspended by a blast of air; second, of an air-tight bed of particles being lifted by air pressure.

In the first case the lifting power of a blast of air is roughly equal to its velocity pressure. For example, a velocity pressure of 0.1 lb. per sq. in. will have a buoyant effect of 0.1 lb. per sq. in. over the surface of the particle. Any particle weighing less than 0.1 lb. per sq. in. of cross-

section will be lifted by this velocity and, conversely, a particle of more than this weight will sink. It is assumed in this discussion that the particles are roughly cubical or spherical and that the area subjected to the action of the air is cross-sectional area. For particles of any other shape, the minimum cross-sectional area should be used, as the particle will assume a position in a blast of air that will bring its long axis parallel with the direction of the air current. It is manifest that the above theory will be somewhat complicated by the eddying air currents, which vary considerably with the shape of the particles. It is presumable that cubical particles would be easier to support than flat slabs or more or less "stream-lined" shapes. The formulas required to figure the lift on a particle are derived from the elementary physical formula

$$V^2 = 2 gh$$

in which

$V$  = velocity of air in feet per second

$g$  = force of gravity

$h$  = head in feet

In connection with this discussion, this formula means that a pressure in pounds per square inch equal to the weight of a column of air 1 sq. in. section and  $h$  feet high will cause air to flow at the rate of  $V$  feet per second. For example, 0.1 lb. per sq. in. pressure at 32° F. and 30 in. of mercury is obtained by a certain height of a column of 1 sq. in. section:

$$\text{Weight of air} = 0.080975 \text{ lb. per cu. ft.}$$

$$\text{Column 1 inch} \times 1 \text{ inch} \times 1 \text{ foot} = \frac{0.080975}{144} = 0.000562 \text{ lb.}$$

$$0.1 \text{ lb.} = \frac{0.1}{0.000562} = 177 \text{ ft.} = h$$

$$V = \sqrt{2 \times 32 \times 177}$$

$$= 106 \text{ ft. per sec.}$$

$$= 6360 \text{ ft. per min.}$$

To calculate the size of coal that will be sustained by this velocity is to calculate the size of particle presenting 0.1 lb. per square inch of sectional area. Using the cube as the shape:

$$0.047 \text{ lb.} = \text{weight of 1 cu. in. coal at 1.3 sp. gr.}$$

$$x = \text{any dimension in inches}$$

$$0.047x^3 = \text{weight of coal particle}$$

$$\frac{1}{x^2} = \text{number of particles covering 1 sq. in.}$$

$$\frac{1}{x^2} \times 0.047x^3 = \text{weight of 1 sq. in. of particles}$$

but the particles weigh 0.1 lb. per sq. in.

Therefore  $\frac{1}{x^2} \times 0.047x^3 = 0.1$

and  $x = 2.1$  in.

Thus a velocity pressure of 0.1 lb. per sq. in. representing a velocity of 6360 ft. per minute will support a 2-in. cube of coal.

Conversely, the velocity required to support any size of particle may be calculated as follows: Assume a  $\frac{1}{2}$ -in. cube of coal

$$\text{Weight per square inch} = \frac{0.047}{2} = 0.023 \text{ lb.}$$

$$h = \frac{0.023}{0.000562} = 41 \text{ ft.}$$

$$V = \sqrt{2 \times 32 \times 41}$$

$$= 51 \text{ ft. per sec.}$$

$$= 3060 \text{ ft. per min. to support } \frac{1}{2}\text{-in. coal}$$

The second factor entering into the stratification of coal by air is the static pressure under the bed. If this bed of coal were so closely packed as to be airtight, the total pressure acting upon it would be the maximum pressure the fan or blower could produce. If a centrifugal fan or blower is used, it is possible to maintain a pressure as high as 8 or 10 in. w.g. and this entire pressure would be exerted to lift and loosen the bed of coal until a certain air velocity could be obtained. The lifting power of this static pressure is quite high and is found as follows:

$$1\text{-in. W.G.} = 5.2 \text{ lb. per sq. ft.}$$

This will balance a solid bed of coal 0.77 in. deep

$$8\text{-in. W.G. will balance } 8 \times 0.77 = 6.16 \text{ in. of coal}$$

A fan of the type usually used, therefore, will provide sufficient static pressure to open up any bed of coal that may be put upon it but usually will not provide sufficient air to support the particles by velocity pressure alone unless the particles are very small.

In the operation of a dry-cleaning table, the air actually used is much less than is required to completely support the particle and the pressure of the air immediately below the coal bed is very low as compared with the maximum pressure the fan will generate. The condition sought is a loosening of the bed so that the refuse will sink and the coal tend to float. To obtain this condition it is necessary to find the balance between the weight of the particles involved and the static and velocity pressures of the air.

#### SEASONAL AND ALTITUDE VARIATIONS OF AIR REQUIREMENTS

Since cold air is heavier than hot air, less of it will be required by volume to support the coal, but velocity pressure will remain the same.



More power is required to move equal volumes of cold air but the requirements of cleaning will remain practically constant, as less of the cold air is required. In rarefied atmospheres, fan speeds should be relatively higher but power should not show much variation.

This discussion of theory leaves much to be desired in the way of a definite basis on which to make calculations but it is hoped that it may suggest some starting points for investigation, which will bear fruit in the form of data and constants which will be useful in the future development of the art of dry cleaning.

### PRESENT STATUS OF DRY CLEANING

A large plant using air cleaning tables is being built and tested at McComas, W. Va. This plant started cleaning coal about the first of May, 1923, and has been operating more or less continuously since.<sup>1</sup> During this time the cleaning tables have operated with entire satisfaction, even exceeding the expectations of the most sanguine enthusiasts. No structural defects have developed and the tables have thoroughly established themselves as highly efficient coal-cleaning devices. However, there have been unforeseen difficulties at McComas which have delayed the successful operation of this plant as a complete unit.

#### *Dust Collecting at McComas and Raton*

The dust-collecting system proved to be inadequate for the large volumes of dust created by this kind of handling of Pocahontas coal. This problem was submitted to the B. F. Sturtevant Co., which installed a complete new system that is now handling the dust in a satisfactory manner. The failures of the original installation at McComas and at Raton, N. M., were due to the fact that the volumes of air handled through the dust-collector system were too small. The Sturtevant system uses large volumes, large pipes, and large collectors, with a power consumption only slightly greater than the original system.

#### *Screens at McComas*

The screens originally installed at McComas were of the anti-gravity type with head motion and details used for the first time on the McComas installation. This type of screen shows certain structural advantages, particularly in its adaptability to level floor design, but it had not been sufficiently developed mechanically to withstand the hard usage to which the screens were submitted and breakage of parts frequently interrupted operation.

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<sup>1</sup> Written in November, 1923.

The vibrators which enlivened the screen surface also gave trouble and inefficient screening so interfered with the operation of the tables and caused the circulation of so much dust in the air, which should have gone to the undersize, that it was decided to replace the screens with Hum-Mer screens, of which the operating characteristics are well known.

### *Other Plants*

There is now under construction a 150-ton per hour dry-cleaning plant at Wyco, W. Va., which was contracted for by the Wyoming Coal Co. after the officials of that company had carefully followed the progress of the McComas plant and had convinced themselves that the difficulties experienced there were capable of solution. This plant is designed and built by the Roberts & Schaefer Co., using American pneumatic separators, Sturtevant dust collector, and Hum-Mer screens. A complete description of this plant will soon be published.

Many operators have declared that they are entirely in favor of dry cleaning and are merely awaiting the satisfactory working out of the details of the accessory apparatus before erecting the necessary plants.

### OTHER DRY-CLEANING DEVICES

A dozen or more new dry-cleaning tables are in course of development. Some are in the experimental stage, some are being transferred to coal cleaning from the field of ore concentration, and one at least is being included in the equipment of a plant under construction. None, however, has been placed on general sale except the American pneumatic separator.

### AMERICAN PNEUMATIC SEPARATOR

This separator has been frequently described in the technical press. Briefly, it consists of a perforated deck through which air is forced by a centrifugal fan. The top of this deck is riffled and reciprocated in the direction of the riffles by a head motion which forces the material forward. A side slope to the deck causes coal to flow over the table to the side, assisted by the air, and the reciprocation of the table causes the refuse to advance to the end of the table between the riffles. This combination of motion and air causes the delivery of refuse on one end, gradually grading into clean coal at the other end.

This separator is capable of cleaning coal as large as 2 in. in diameter and as fine as 100 mesh, by using the proper deck for the size treated. The coal is first sized so that the finest particles in the feed are about half the diameter of the largest, to get the best effect. The capacity of the table varies according to the size of the coal; coal about 1 in. in diameter has the highest capacity, about 25 tons per hour. The power

required to operate the table, including fan, head motion and feeder, also varies according to the size of coal and the capacity and has its maximum at about 25 horsepower.

The American pneumatic separators are designed and manufactured by Sutton, Steele & Steele, Inc. of Dallas, Texas, for many years makers of dry-separation devices, and marketed by the American Coal Cleaning Corp., which has an exclusive right on these separators for the treatment of coal.

The cleaning tables at Raton, N. M. were manufactured by Sutton, Steele & Steele and sold directly to the St. Louis, Rocky Mountain & Pacific Coal Co. before the American Coal Cleaning Corp. was organized. They are of a smaller type than the so-called American pneumatic separator, being designed primarily for seeds, grains, and ores, but are fully as effective except that they have a lower capacity. The American pneumatic separator, with its higher capacity and other features peculiar to coal cleaning, was designed by Sutton, Steele & Steele at the request of the cleaning corporation. This type of separator was installed at McComas and also at Wyco.

### *Sizing*

In all of the tests made on this separator, the coal has been prepared for cleaning by a preliminary screening into several sizes. This practice has been followed at the Raton and McComas plants in order to secure the best possible cleaning. Given the advantage of close sizing and middlings return, the pneumatic table will closely approach perfect cleaning on the sizes treated. By perfect cleaning is meant the complete removal of all material heavier than a certain predetermined specific gravity, with the loss of none of the lighter particles into the refuse. This perfect cleaning may not produce a clean coal with as small an ash content as may be desired, but if not, it is the fault of the coal and not of the cleaning.

If this perfection of cleaning is not required and it is desired merely to remove a portion of the heavy material, it can be done with the dry-cleaning tables without such close sizing. Also, those coals which have small proportions of bone coal and other constituents of intermediate specific gravity will require less attention to sizing than coals with much of this material.

For proper dry cleaning, therefore, close sizing is essential to get efficient cleaning but a considerable reduction in ash can be accomplished without it.

### *Dry Feed*

For the most efficient screening into the various sizes, the feed should be reasonably dry. Coal that is dampened by moisture other than

"inherent" moisture screens with difficulty and carries much of the fine clinging material into the oversize. This is no great detriment to table operation except that it cuts down table capacity by subjecting much material to treatment which receives no benefit. Coals which contained as high as 12 per cent. moisture have been treated on these tables with good results. It may be said, therefore, that any coal that can be screened can be cleaned. Thus the matter of moisture in the coal becomes purely a screening problem, and even should the coal be screened by wet screening, with sprays, the sized products may be subsequently tabled.

### *Middlings Disposition*

On the American separator, the various products are in plain sight and can be easily directed into clean coal, middlings, or refuse chutes, or as many different grades of coal as may be desired, by a very simple adjustment. The present practice is to return the middlings to the feed, the purpose of this being twofold; first, to allow "accidental" middlings another opportunity to find their proper zone; second, to take care of any fluctuations in the refuse content of the feed. With this practice, the operator is not required to shift the divider with every variation of the refuse line.

Another advantage of this graded discharge is the possibility of adjusting the products to suit various market conditions. Portions of high-grade coal may be taken off to fulfil rigid specifications by either wasting a certain amount of the inferior grades of coal or making separate disposition of them. The use of a large amount of intermediate coal for steam around the plant will improve the remainder of the slack destined for shipment; in fact, the more of this that can be used, the better is the boiler fuel as well as the shipped portion.

### RESULTS OF DRY-CLEANING TESTS

Many coals have been tested on dry-cleaning tables with uniformly satisfactory results. Table 1 shows some actual tests made on representative coals; Table 2 shows results at Raton. The tables used at Raton are small in size but the quality of the cleaning is representative.

TABLE 1.—*Tests on Dry-cleaning Tables*

KIND OF COAL	NO. OF TESTS CONDUCTED	PER CENT. ASH		PER CENT. REDUCTION
		CRUDE COAL	CLEAN COAL	
No. 3 Pocahontas seam.....	18	10.04	5.37	46.51
No. 6 Illinois seam.....	4	13.37	6.93	48.17
No. 4 Indiana seam.....	4	11.15	6.79	38.69
Clinchfield, Va.....	1	11.64	4.63	60.22
No. 5 Ohio.....	1	19.95	8.25	58.70
Penna. anthracite No. 2 buckwheat	1	18.70	8.50	64.30
Coke breeze.....	1	17.37	9.54	46.23

TABLE 2.—*Dry-cleaning Results at Raton\**

SIZE OF COAL	RAW COAL	PER CENT. ASH CLEAN COAL	WASTE
1 in.— $\frac{3}{4}$ in.	17	11	63
$\frac{3}{4}$ in.— $\frac{1}{2}$ in.	17	10.5	65
$\frac{1}{2}$ in.— $\frac{3}{8}$ in.	16	9.5	70
$\frac{3}{8}$ in.— $\frac{3}{16}$ in.	18	10	66
$\frac{3}{16}$ in.— $\frac{1}{16}$ in.	22	14	70
$\frac{1}{16}$ in.—60 mesh	25	19	70
Total.....	16.83	11.06	64.6

\* From paper read by Frank Young before Rocky Mountain Coal Mining Institute.

Difficulties have interfered with the continuous operation of the plant at McComas, therefore the average analyses of the products would fail to express what is possible to accomplish when the plant is operating properly. The figures in Table 3, therefore, were selected from the actual results, which will no doubt be improved upon in the future.

TABLE 3.—*Selected Data on Results at McComas*

SIZE OF COAL, INCHES	RAW COAL	PER CENT. ASH CLEAN COAL
2 — $1\frac{1}{2}$	15.8	6.5
$1\frac{1}{2}$ —1	18.9	9.3
1 — $\frac{1}{2}$	9.0	6.4
$\frac{1}{2}$ — $\frac{1}{4}$	9.0	6.6
$\frac{1}{4}$ — $\frac{1}{8}$	8.7	6.5
$\frac{1}{8}$ — $\frac{1}{16}$	9.1	7.6

### CONCLUSION

Sufficient progress has been made to insure the dry-cleaning process an important place among the established coal-cleaning methods. Results at McComas and other installations have indicated that the important units involved in the process—the tables themselves—have given a satisfactory demonstration, and it only remains for those who are exploiting this method to develop the accessory devices, to acquire more detailed information as to the sizing requirements, and to inform the public of the possibilities of the method to bring about a vast improvement in the methods of cleaning nut and slack coal.

### DISCUSSION

RAY W. ARMS (written discussion).—The plant of the Wyoming Coal Co. at Wyco, W. Va., is a dry-cleaning plant using American pneumatic separators. The No. 3 Pocahontas seam at this point contains several inches of bone coal, which has a middle band or core of very high

ash material that grades gradually, and with no distinct line of separation, into the usual low-ash and high-quality No. 3 Pocahontas coal. The coal in the outer edges of this bone band, in appearance, is almost exactly like the best coal, which makes it quite impossible to remove, in the mine, anything but rock and a small amount of the heaviest of this bone.

The coal is brought to the surface, screened at  $1\frac{1}{2}$  in. and the lump hand-sorted over picking tables, to remove as much of the bone coal as possible. After picking, the lump and slack are, usually, reassembled in the form of picked run-of-mine, as it is to that trade that this mine, and in fact, a large part of the territory tributary to the Virginian Railroad caters.

It soon became evident, however, that so much of the ash of the resultant coal was caused by the slack, which could not be hand picked, that it would be necessary to provide some means of mechanical separation.

W. P. Tams, president of the Wyoming Coal Co., conducted tests on various cleaning devices and decided that the best results could be obtained by installing a Bradford breaker, in which the larger lumps of hand-picked bone could be shelled from the adhering coal, and a pneumatic cleaning plant, which would handle all the slack as well as the crushings from the Bradford breaker. This cleaning plant was expected to remove all rock and those poorer grades of bone coal that kept the ash in the slack above the desired figure.

The plant was designed and built by the Roberts & Schaefer Co., using a Pennsylvania Crusher Co. Bradford breaker, Link-Belt elevators and conveyors, Hum-Mer screens, Universal Re-Screens, American pneumatic separators and a B. F. Sturtevant Co. dust-collecting system. The plant, of timber construction, is built adjacent to the tippie and delivers its cleaned product back to the tippie.

The first separation is breaking down the big lumps of bone coal in the Bradford breaker. The crushings from this go to the cleaning plant and the reject directly to a rock bin. The slack from the tippie, together with these crushings, go direct to the foot of a bucket elevator, capable of handling 175 tons per hour, which raises them to the top of the dry-cleaner building, whence they go through the succeeding operations by gravity.

A cross conveyor takes the coal from the elevator and distributes it to the top of a tandem series of four Hum-Mer screens, each of which drops the undersize to a pocket and delivers its oversize directly to the succeeding screen. These screens divide the coal into the proper proportions and the proper sizes for the pneumatic separators. The undersize from the first of these screens is delivered to a second set of four screens, which separates the fine coal into the sizes to be tabled. The finest of these screens is  $\frac{1}{16}$  in., the undersize of which is bypassed

without further treatment to the slack coal. All screened products, except these fines, are run into five hoppers, of 4 tons capacity each, feeding the pneumatic tables. Attached to the bottoms of the bins are fine Universal re-screens, which screen the products and remove the fine breakage occurring in the bins. These screens not only improve the operation of the table but reduce the dust, which otherwise would be blown about on the table floor by the air passing through the tables.

The re-screens feed to the five American separators, which grade the coal in a line of discharge varying from the heaviest refuse, at one end, to the best coal at the other. This line is divided into finished refuse, which is discarded, cleaned coal, and middlings, which are returned to the boot of the elevator for retreatment through the plant.

The finished products are collected on a single two-compartment gathering conveyor that, on one strand, takes the cleaned coal to the tipple and the middlings to the elevators and, on the other strand, delivers the refuse to a bin and the middlings, if desired, to a separate bin.

To control the dust, care was exercised to keep the fine coal at all times under cover so that dust could not escape. With this end in view all conveyors, chutes, and elevator were covered. Over the tables, where air tends to circulate the dust, are placed dust hoods with suction provided to remove all the air from the covered area and a surplus to insure that all dust is removed by the hoods. The covered area varies from about 5 to about 90 per cent. of the table surface, depending on the fineness of the coal and the tendency to produce dust. Suction is also placed on all hoppers leading from the screens to avoid boiling up of the dust clouds during screening. All the dust laden air from these various sources goes through a fan to a cyclone collector, which removes the dust and delivers it to a covered screen conveyor, which returns it to the slack.

The Wyco plant started operations Feb. 1, 1924, and has been running continuously since. It is too early to state what the actual results of the operation will be as the organization and training of the operation crew and the adjustments always incident to the starting of a new plant have occupied the time, so far. From the few days of operation, however, it is apparent that refuse and bone are being effectively removed from the coal with a minimum of operating expense.

S. A. TAYLOR, Pittsburgh, Pa.—Have you any of the figures of the McComas plant, showing the effect of the electrical precipitation of the dust?

RAY W. ARMS.—Mr. Nesbitt of Pittsburgh undertook some experiments there. He planned to use electrical precipitation, but after he got to the plant and examined it, he made all of his experiments on mechanical precipitation. His mechanical collectors accomplish the purpose entirely by baffles.

HOWARD N. EAVENSON, Pittsburgh, Pa.—Some of the members question the statement that the clean ran from about 95 to 98 per cent. of the coal.

RAY W. ARMS.—Those figures are from tests made at Dallas and at the Ohio State University. By perfect coal cleaning, we mean the complete separation of a mass of coal at a definite specific gravity, that is, putting into one pile, which we call refuse, all of the material above that definite specific gravity, and putting into the clean coal pile all of the material below that gravity.

We do not claim perfect work. There is no device, probably, that can produce absolutely 100 per cent. results. We have shown, on tests, however, anywhere from 95 to 98 per cent. of perfection with a careful screening; that is, the clean-coal product has been 95 per cent. above a certain gravity, which we will say is 1.45, and 5 per cent. only was heavier. Also on the refuse side, a similar percentage has been lighter than 1.45.

W. R. CRANE,\* Birmingham, Ala.—Is that without retreatment of the middling product?

RAY W. ARMS.—No; that is with retreatment of the middling product. There is a zone, which we term middlings, that consists not only of true middlings (that is, of actual combined particles) but of the accidental middlings (dovetailed zone of clean coal and actual refuse). If that is returned to the feed, which is a simple process, the perfection of cleaning can be approached closely. Without the return of the middlings we have no test. The clean coal in that case would probably run around 85 or 90 per cent.

F. F. JORGENSEN, Gillespie, Ill.—Can you give the cost, per ton, of this bituminous plant for a ton of raw stuff treated?

RAY W. ARMS.—That would be a little unfair, at this time. We had a year of development work, during which much equipment has been removed and replaced. A large part of that cost has been applied to coal production and cleaning by the coal company, largely because no appropriation had been made for changes so that the books would show tremendously high treatment costs.

We have worked out the costs by taking off power and labor items that could be chargeable directly to coal cleaning. The power costs were in the neighborhood of 3 cents per ton. The labor cost has not been made, as a unit, but we would charge three men's time only to the actual cleaning, that is, exclusive of taking care of refuse, loading coal, and delivering coal to the cleaner, the actual labor inside the cleaner is three men's full time.

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\* Superintendent Experiment Station, Bureau of Mines.



F. F. JORGENSEN.—What rate per day are they paid?

RAY W. ARMS.—Two of them are paid \$6.50 and the other \$10 a day.

F. F. JORGENSEN.—It takes only three men to operate that?

RAY W. ARMS.—Yes, that is actual full time on daily operation. Perhaps adding the few laborers who come in occasionally you could increase that number to four, to be conservative.

F. F. JORGENSEN.—Does it run 1200 tons a day with these three men?

RAY W. ARMS.—Yes; that is all it takes, one on the screen floor, one on the table floor, and one in general charge. That is exclusive of labor of repair, which is a sort of indeterminate item so far which cannot definitely be itemized. Right now the repairs are negligible as there is no regular repair crew. There was a repair crew of six or eight men before the machinery was changed to the present type, but now repairs are made as needed, usually by the operating crew. The Wyco plant is now using three men, but it is expected later to use only two.

F. F. JORGENSEN.—There are eight tables in the plant?

RAY W. ARMS.—There are eight tables and thirty-six units of screens; we call a 4-ft. section one unit. That plant was intentionally overscreened so that we would be sure to have plenty of screen surface.

G. R. DELAMATER, Harrisburg, Pa.—All of the first difficulties of the McComas plant were with the screening of the coal. There is no doubt that the tables make a complete separation, producing a satisfactory clean coal and a satisfactory refuse; that is, refuse free of coal. In about ten months' operation, most of the difficulties on the tables were the result of lack of proper preparation of the coal by the screens, and by putting thirty-six units of Hum-Mer screens into this plant, the coal company wanted to feel sure that it could operate daily without interruption. The company intends to build additional dry cleaning plants and thought that any surplus screens in the Crane Creek plant could be used in the second plant.

The McComas plant is based on 240 tons an hour and the Wyco plant on 150 tons an hour with a circulating tonnage of about 15 tons of middling, making a total of 165 tons an hour. At Wyco, with that 165-ton basis, there are sixteen Hum-Mer units. While that plant had only been in operation about a week when I was there, the screen equipment seemed to be about right.

The cost of cleaning coal with the dry process will depend largely on the preparation of the coal for the tables. Practically every mine that I have been in has more or less wet coal, but we have had no serious trouble in handling wet coal at these two plants, down to and including

the  $\frac{1}{8}$ -in. screen. On the  $\frac{1}{16}$ -in. screen, if the coal is so wet that the slack, if crushed in the hands, will stick together, it will give trouble; but a lot of that difficulty can be avoided by attention to the method of getting rid of the water in some of the places, or by mixing the cars of wet slack coal with dry coal.

My opinion would be that the final cost would be about the same as for wet-coal cleaning. It may be a little lower, but I do not think that either of the plants that have been in continuous operation (Crane Creek and Raton, N. Mex.) were working properly (and that refers to both screening and dust collection) long enough to give definite figures. At this stage, while we have hopes of lower costs, it is better to figure that the cost will be about the same as for wet washing.

One thing I noticed at both McComas and Wyco was that a table getting too light a load would not do as good work as a table that was heavily or normally bedded. It would be better in many cases to use a larger range of sizes on the table and have it bedded properly than to try to work with a close sizing with light bedding.

The refuse discharge of the tables I have seen is very clean, very free from coal, provided they circulate the middlings. In our Hum-Mer screen work, this is the first time we have had an opportunity to classify coal to so many sizes [in one] operation and attempt to get a high efficiency of screening. We have not gone far enough in this work to say just what the efficiencies are, but when the coal is reasonably dry, or dry enough so that it does not stick together when crushed in the hand, we can get high efficiency in screening and entirely satisfactory for the dry concentration work.

F. F. JORGENSEN.—The dry washery plants are located right at the coal mine?

G. R. DELAMATER.—They are.

F. F. JORGENSEN.—Then when the mine would have to ship the cars in wet weather, it would seriously affect the screening?

G. R. DELAMATER.—It would seriously affect only the  $\frac{1}{16}$ -in. size. We have a 4-ft. tandem Hum-Mer screen installation making nut coal and slack at the Mount Union tippie of the East Broad Top Railroad & Coke Co. That coal is mined in the Broad Top district, is hauled about 35 miles in open-top cars, and sometimes it gets quite wet. We put in two screens, 4 ft. wide and 5 ft. long, bolted end to end, and for a year have been handling 180 tons per hour, using 1 hp. The cloth on both screens is  $1\frac{1}{8}$  in. clear opening square mesh. These tests of the products are made on a  $\frac{3}{4}$ -in. round-hole test screen; 9 per cent. of the nut coal, or over-screen product, is undersize, of which 7 per cent. is over a  $\frac{1}{2}$ -in. screen and only 2 per cent. through the  $\frac{1}{2}$ -in. The slack coal is showing from 4 to  $4\frac{1}{2}$  per cent. oversize.

We use a heavy vibration on the  $1\frac{1}{8}$ -in. cloth in the first unit and nothing over  $\frac{1}{2}$  in. passes through this screen. We have to put 70 per cent. of the feed coal through our cloth, which so crowds the meshes that it does not let the larger sizes get through. Then, by adjustment of the vibrator on the second unit, we use a light vibration on the second screen, and as considerable tonnage has been eliminated through the cloth of the first unit, the second screen has a lighter tonnage to handle, which permits bedding the coal on this screen for better elimination of the larger sizes. At times the coal is very wet, but we have experienced no difficulty in handling that wet coal with high screening efficiency. From what I have seen at McComas and Wyco, I believe that we can handle sizes down to and including the  $\frac{1}{8}$ -in., even with coal that is rather sticky, but I do not think, with sticky coal, we can handle the  $\frac{1}{16}$ -in.

RAY W. ARMS.—At McComas, we have run for nearly a year and occasionally about a hundred cars of the coal stand in the mine yard overnight. Several times it has rained quite hard, but usually the rain did not penetrate the coal in the car more than 12 or 18 in., which got sufficiently mixed so that it caused little difficulty.

The coal that gives the most trouble is that which is soaking wet when it comes from the mine; that is, mined from a wet place, or, as at Wyco, had stood in  $3\frac{1}{2}$  ft. of water and was drawn through that water when going to the tipple.

The actual figures on the moisture in the operation I am not prepared to give, but we ran one test on Canadian coal at Dallas, during which a condition was that the coal should be wet to 12 per cent. moisture before testing. The normal inherent moisture of that seam underground is from  $2\frac{1}{2}$  to 3 per cent., so that we were required to add 8 to 10 per cent. of actual wetness. They conceded that dry tables could clean their coal when it was dry but they wanted to see what could be done when it was wet. We were able to screen to  $\frac{1}{4}$ -in. with good screen efficiency. Those  $\frac{1}{4}$ -in. particles had clinging to them fine pieces of coal, which represented, on a dry-screening test, roughly 8 per cent. At  $\frac{1}{8}$ -in., about 20 per cent. of fine particles were clinging to the larger pieces. At  $\frac{1}{16}$ -in. the undersize was 50 per cent. or over. Now, at  $\frac{1}{16}$ -in., that is, from  $\frac{1}{8}$  to  $\frac{1}{16}$  in. in size, the tables had difficulty in cleaning. Refuse was removed, to be sure, but that refuse did not represent the entire amount of refuse in the sample. At  $\frac{1}{8}$ - to  $\frac{1}{2}$ -in., as determined by chemical analysis, the refuse line did represent the entire amount of refuse in the coal; that is, it was practically all removed, and of course the sizes from there up were thoroughly as representative as on dry coal.

So wet coal is purely a screening problem and not a tabling problem. With good screening, even though that screening is done on a wet screen, we can get just as good table results as on dry coal. The only thing needed is to give it a little more air on the table to break up the bond

created by the moisture. That is accomplished by a mere adjustment of the table.

G. R. DELAMATER.—I do not want to give the impression that at the McComas and Wyco plants the tables failed to make separation because of moisture. The statement that even though the screening on the  $\frac{1}{16}$ -in. was inefficient when the coal was wet and sticky, all the work on the coarser sizes was just as good as it had been on the dry coal, is correct.

The screening troubles were not in the coarser sizes; and even when this wet coal, of the  $\frac{1}{8}$  by  $\frac{1}{16}$ -in. size went on the tables and the particles stuck together, resulting in poor elimination of the minus  $\frac{1}{16}$ -in. coal, we could make a good separation; such separation, though, will not be as perfect on those fine sizes as it would be on dry coal.

At the Steelton plant of the Bethlehem Steel Co., we installed some Hum-Mer screens using  $\frac{3}{16}$  in. clear opening cloth, with the intention of screening out all minus  $\frac{3}{16}$ -in. coal. That plant gave efficient screening for about  $3\frac{1}{2}$  to 4 years even on coal of high moisture content, all the coal being hauled from the central Pennsylvania district.

A year last summer we equipped the coal washery of the Woodward Iron Co. at Woodward, Ala., with  $\frac{3}{16}$ -in. Hum-Mer screens. In a letter written about a month ago, Mr. Boynton, the general manager, stated that the screening had been very satisfactory; the efficiency had been in excess of 90 per cent. at all times. This coal is hauled for some distance to the washery in open-top cars. The company has been using 60 or 70 railroad cars a day for storing wet washed coal, so that the coal could drain before it went to the coke ovens; the installation of the  $\frac{3}{16}$ -in. screening plant eliminated the use of those cars, greatly reduced the moisture content of the coal, increased the capacity of the coke ovens, and reduced gas consumption.

F. F. JORGENSEN.—What is the average reduction in ash content of the coal at the two plants you speak of?

RAY W. ARMS.—At McComas, the average reduction at present is 4 per cent., from 12 to 8 per cent. in the slack. On the individual sizes, nut coal for instance, the average reduction is about 10 per cent. Nut coal is dirty, coming to the cleaner at 16, 18 and sometimes 20 per cent. ash and being reduced to 6 or 7 per cent. The figures selected here are about 16 per cent. That particular sample runs 6.5 per cent. on the clean coal, or 9.3 per cent. reduction, whereas in the finer sizes of the slack there is not so much dirt to start with on the Pochahontas coal and the average reduction is about 4 per cent., including the material that is not treated at all.

F. F. JORGENSEN.—What passes through the  $\frac{1}{16}$ -in. screen is not treated?

RAY W. ARMS.—No, merely screened out.

F. F. JORGENSEN.—All coal above  $\frac{1}{16}$  in. is treated?

RAY W. ARMS.—Yes; from  $\frac{1}{16}$  to 2 in. The  $\frac{1}{16}$ -in. material runs practically always less than 10 per cent., usually about 9 and a fraction. When mixed back with the other clean material, it produces an average of less than 8 per cent.

F. F. JORGENSEN.—What percentage of the total of raw coal is this  $\frac{1}{16}$ -in. product?

RAY W. ARMS.—At McComas, it is very high; over 25 per cent. of the slack is smaller than  $\frac{1}{16}$  in.

## Coal Mining by the V System

By GLENN B. SOUTHWARD,\* E. M., ELKINS, W. VA.

(New York Meeting, February, 1924)

THE V system of mining used at the Norton mine of West Virginia Coal & Coke Co. was designed as a modified long wall with face conveyors, for use under roof conditions that would not permit regular long-wall

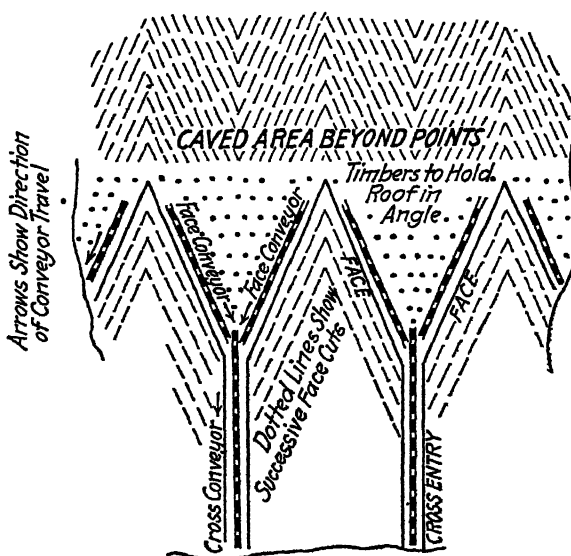


FIG. 1.—GENERAL DESIGN AND ARRANGEMENT OF FACES IN V SYSTEM.

methods. This mine is in the Lower Kittanning seam, which averages about 6 ft. in height. There is from 20 to 30 ft. of slate and shale immediately over the coal and above this is a bed of sandstone 40 ft. or more thick; the total cover will vary from 50 to 250 ft. In the room-and-pillar workings, the top in the rooms and headings is generally good but it is

\* Chief Engineer, West Virginia Coal & Coke Co.

comparatively easy to break when the pillars are being drawn. This was not thought suitable for regular long-wall mining, which led to the design of the V system. It was also thought that while long-wall methods could be studied and taken as a guide, the procedure in the V system would have to be determined by experiment.

The design primarily consists of a pair of comparatively short faces arranged at an angle to each other so as to form a V, both of these faces being turned from a single entry the line of direction of which bisects the angle of the V. Two or more of these pairs are connected in parallel and form a double or multiple V arrangement, as shown in Fig. 1. In mining, machine cuts are taken along the faces so that the central angle remains constant and the points stay in line; and as mining progresses, the faces retreat and assume the successive positions shown by the dotted lines. The fundamental idea of this design is to give maximum protection to the working faces by supporting the roof across the angle between the faces and leaving it free to cave or subside in the mined area beyond the points. If the roof over the angle is considered as a beam supported at each end by the solid coal in the points, the length of span possible will depend on the character of the roof. The depth of cover will determine the amount of coal necessary to support the ends of such a beam and this will fix the degree of the central angle. It is hardly probable that the dimensions best suited to any particular roof condition can be determined except by experiment.

#### EXPERIMENTAL PERIOD

The design was perfected in the summer of 1921, by the writer, and a trial face was started in December of that year; this was intended mainly as a test on the mechanical equipment and preliminary experiment on roof action. During these experiments, development was started for the V system but, because of the six months' interruption by a strike, mining on the V faces was not begun until late in 1922. The trials on the V system continued through an experimental period of several months and by March, 1923, it was considered that an operating system had been devised. Since that time, there have been no changes in the general method, except in operating details to increase efficiency and reduce cost.

It is not necessary to describe, in detail, the different methods and trials made during the experimental period; though it may be pertinent to say that straight faces were tried and failed. The first trials on the V system were with faces 100 ft. long and a central angle of  $90^{\circ}$ ; this makes a span of 140 ft. from point to point. With these dimensions, the beam effect was not obtained; the span was too great and the roof action was practically the same as when straight faces were reused. It

was some time before this fact was fully accepted because there was always the possibility that the failures on the 90° angle were caused by ineffective timbering or improper methods. Several procedures were used and each one thoroughly tried; these involved different sizes and spacing of posts, cribs, and packwalls, also different timing of roof falls. Falls were tried over large areas and small areas, but the results were practically the same in every case—the top fell inside the points and along the faces. When it was decided that the failures were the result of too wide a span, the angle was changed to 45° with 85-ft. faces, making a span of 80 ft. across the points; the results proved that these were

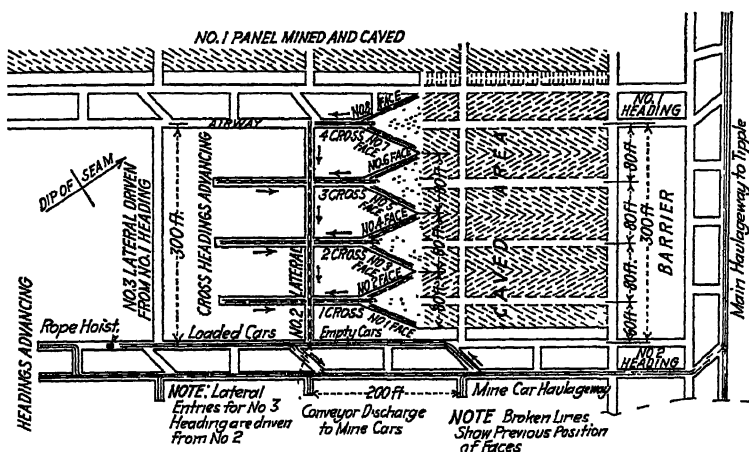


FIG. 2.—ARRANGEMENT OF CONVEYORS.

apparently the proper dimensions. One pair of faces was first tried and worked successfully; the number of faces was then increased to two pair, then to three, and finally to four pair, as shown in Fig. 3, which is the number now being used.

### PRESENT MINING SYSTEM

The present operating system consists of a panel of eight faces each 85 ft. long, as shown in Fig. 2. Each pair of faces is tributary to a single cross entry and the cross entries are driven at 80-ft. centers off a lateral entry. These laterals are spaced 200 ft. apart and are the headings from which the cross entries are developed and through which the coal from the faces is transported to the haulageway. Mining is done by slab cuts on the faces and as all faces are worked at the same time, the direction of retreat is at right angles to and toward the lateral entry. The advance cross entries are driven at the same speed as the



faces retreat, so that by the time the angle, or intersection, of the faces has retreated to the lateral entry, the cross entries have been driven through to the next lateral and the coal is taken out to the haulageway

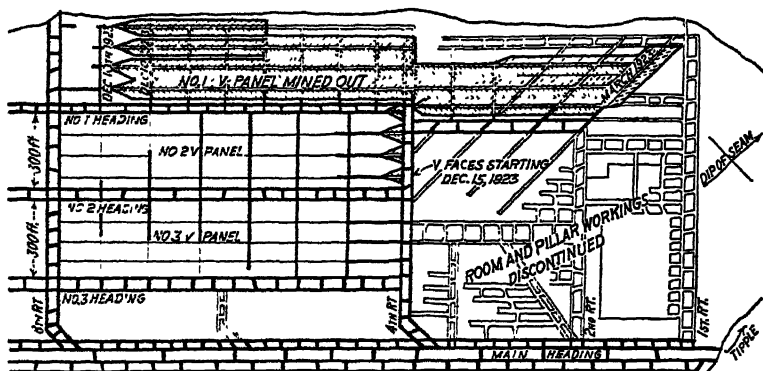


FIG. 3.—COAL MINING BY THE V SYSTEM.



FIG. 4.—FACE CONVEYOR BEING MOVED FORWARD IN A COMPLETE UNIT, WITH POST PULLERS.

through it. Only a limited amount of advance work is required. Actually, this is an advancing system, as far as development is concerned, but the faces are always strictly retreating. It is, of course, possible to make the entire system retreating by first driving the haulageway to its barrier limit.

## CONVEYOR SYSTEM

All transportation from the face to the haulageway is by a system of conveyors, known as the "Movor." This is a steel-pan belt type, made in standard interchangeable sections, each 6 ft. long, so that an assembly may be made of any desired length. Power is applied through drive sections, which are self-contained electric-motor drives; these are interchangeable with the straight sections and can be located at any point, or at two or more points, in the conveyor. The same standard parts are used on the face, cross, and lateral conveyors in the V system; the different carrying capacities required of these units are obtained by regulating the speed through a system of gears in the drive section. The

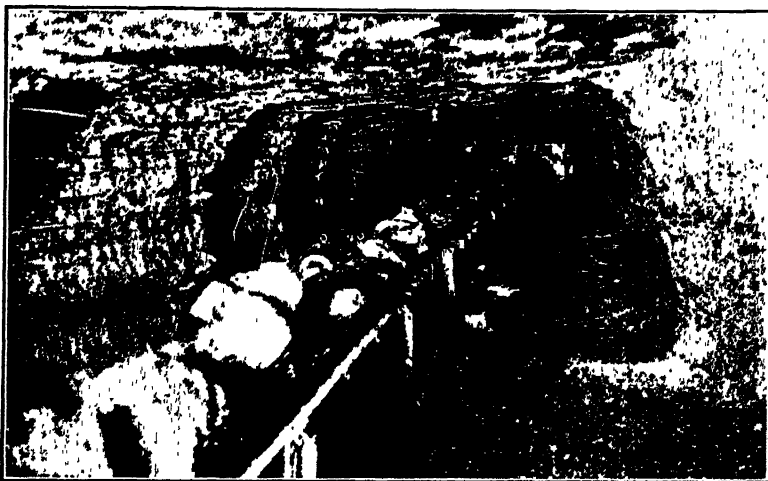


FIG. 5—CROSS-ENTRY CONVEYOR, SHOWING DISCHARGE END OF FACE CONVEYORS IN BACKGROUND.

frames and pan belt are connected by key bolts and cotter pins, so that a very short time is required for removing or adding sections. Because of the multiple-drive feature, all parts are made comparatively light and are easily portable; in fact, the 75-ft. face conveyors are moved in a complete unit with post pullers, see Fig. 4.

The installation is shown in Fig. 2. Along each face, there is a face conveyor into which coal is loaded by hand and each two adjacent face conveyors discharge on to a conveyor laid in the cross entry; see Fig. 5. The four cross-entry conveyors discharge to one lateral conveyor in the lateral entry, which, in turn, loads into mine cars on the haulageway. In this manner, all the coal from the eight faces is collected and loaded into mine cars at one discharge point. Mine cars are handled in 25-

car trips direct from the tippie to the loading point by an electric locomotive. The cars are moved in a solid trip under the conveyor discharge by a rope hoist, controlled at the discharge point, and are not uncoupled during the loading; neither is the conveyor stopped between cars, see Fig. 6. One operator controls the trip movement during loading and operates a small hinged chute, which prevents spillage between cars.

The haulageway and the lateral entries are developed with mine cars and the cross entries are advanced with conveyors. After each cut is loaded, the face conveyors are moved forward and the cross entry is correspondingly shortened. Sections of the cross conveyor that are

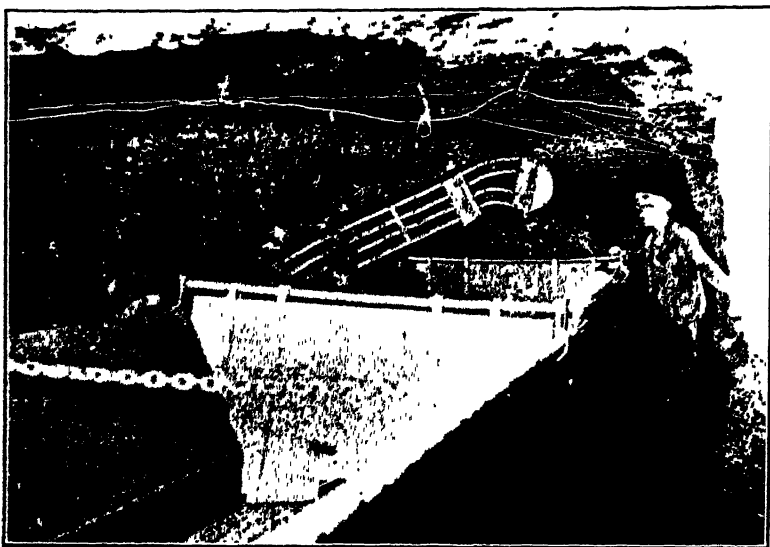


FIG. 6.—DISCHARGE END OF LATERAL CONVEYOR LOADING TRIP OF MINE CARS.

removed are used to extend the conveyors in the advancing cross entries. When the face entries have retreated so that the angle of the faces has reached the lateral entry, the lateral conveyor is removed to the next position ahead. As it is customary to move this conveyor in about 12 hr., there is no interruption in the regular daily operation of the faces at that time.

### ROOF ACTION

The territory that has been mined out since March, 1923, is shown in Fig. 3; it comprises an area 2000 ft. long and varying from 200 to 300 ft. in width as the number of faces were increased. During this mining, falls have occurred across the entire area on an average of one every 60 ft. Timbers are set behind the face conveyors, after each cut,

and are always maintained in the area between the faces to support the slate immediately over the coal; but at more or less regular intervals, they are removed from the area beyond the points and the top permitted to fall. The falls do not generally come inside the points to any extent, except where the top is weak. At such times, the face conveyors are shortened to a point of safety and mining is not interrupted; the output is decreased for only one or two days, as the faces are lengthened on each succeeding cut after the fall and soon regain their full length.

This panel is worked parallel and close to the outcrop and the outside faces are, therefore, under very light cover. Where this condition exists, the top is considerably weakened—probably by weathering—and would not span the entire distance across the angle. Consequently, the length of span was decreased on the two outside pairs by shortening the faces, which left a narrow pillar unmined. With this exception, the recovery has been high and the amount of coal left in this narrow pillar between the two outside faces was less than would have been lost in room-and-pillar mining under the same conditions.

#### OPERATION

The schedule of operation is arranged to give a complete cycle every 24 hr., using two regular 8-hr. shifts. The day shift loads the coal from the faces. This is done by hand; the loaders shovel the coal, which has been previously shot down, on to the face conveyors, which take it without further attention to the mine cars. The night shift does the cutting, drilling, shooting, timbering, moves the face conveyors, shortens the cross conveyors, and, when necessary, removes timbers to bring a fall. So far, there has been no great difficulty in maintaining this schedule and little time has been lost by reason of the failure of either shift to complete its work.

The amount of coal produced from the eight faces will average about 750 tons per day, not including development. All labor rates paid in the V system are on a time basis; the average number of men regularly employed, from the faces to the tippie, are as follows:

Day shift:	32 loaders
	1 hoist operator
	1 electrician
	3 mechanics
	2 motorman and brakeman
Night shift:	4 machine runners and helpers
	2 drillers
	1 shot firer
	12 timbermen
	2 mechanics

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Total: 60 men

This list does not include the day and night foremen but does include a "straw boss" on each pair of faces, who works as a loader but is an experienced miner and directs the face work. Each loader will average about 25 tons of coal per shift loaded on to conveyors. This, however, is in addition to handling a heavy slate parting 8 to 12 in. thick occurring 2 ft. above the bottom of the seam. This must be broken up and shoveled or thrown across the conveyor and gobbled between the timbers. The work required for this takes from 25 to 50 per cent. of the loader's time and, of course, reduces by this percentage the tonnage that each man would load if the seam were clean.

### ALL-CONVEYOR MINE

The plan described is a combination of conveyors and mine cars, but it is doubtful if this is the most efficient or the most desirable arrangement. A plan is now under consideration, and experimental work on it is being started, to extend the conveyor system all the way to the tippie, thus eliminating all mine-car haulage. Because of the increased output per employee and the consequent reduction in number of houses required, also by the elimination of all track, haulage and gathering locomotives, and reducing the number of mining machines and pumps, it has been estimated that the cost of installing an all-conveyor mine should be from 25 to 40 per cent. less than that required for a room-and-pillar mine of the same output. This, however, is mainly theoretical at this time.

### SUMMARY

In comparing the V system of mining with other methods in general use, the question of cost is of primary importance. Without submitting any figures, it can be stated that the output per man employed is much higher than that ordinarily obtained in room-and-pillar methods and the cost of producing coal is correspondingly lower. The reasons for this are apparent. In the first place there is a high degree of concentration. This, of course, is true of most long-wall work but, because of the angle of the V faces, 600 ft. of working face is obtained in an area 300 ft. wide. This concentration simplifies supervision, drainage, and ventilation and reduces the cost of these items to a very low figure. As the main-line locomotive handles the trips from the conveyors to the tippie, this eliminates gathering altogether with a consequent reduction in the operating and maintenance cost of haulage. With 600 ft. of working face, there are eight separate operating units and an interruption on any one of these faces does not affect the operation of the others; whereas in a long single face a fall or other interruption may stop the entire output until the trouble is removed. In case a fall should occur within any angle so as to close a face completely, it would not be necessary to

re-open this as the coal in the point could be recovered by lengthening the adjoining face on the next cross entry. In other words, referring to Fig. 2, if a fall closed No. 3 face, No. 2 face could be extended to mine the point between No. 1 and No. 2 cross entries until the fall was passed.

It is claimed for this system that, where conditions are suitable, a high efficiency in operating and a maximum recovery of coal are possible. However, before any plan of mining is worth serious consideration it must be shown that the methods are safer and that the working conditions are improved. It is believed that this has been accomplished. Working in groups tends to promote a feeling of security and satisfaction among the men, adequate ventilation, proper drainage, and electric lights are all easily provided, the working faces are under close and competent supervision and inspection at all times, the explosives are handled by experienced men only, and there are no trolley wires or car haulage at or near the working faces. These conditions are believed to be mainly responsible for the very low accident record obtained so far and the apparent contentment of labor that has been evidenced in the "V" system during its operation.

## DISCUSSION

MEMBER.—How do you pay your men for loading?

GLENN B. SOUTHWARD.—Everything is on time basis.

MEMBER.—How many men do you have loading across one of the diagonal faces?

GLENN B. SOUTHWARD.—From four to five, depending on the length of the face. Our loaders are so arranged that each will give about twenty-five tons per loader a day.

MEMBER.—How much timber do you use?

GLENN B. SOUTHWARD.—A little more than will be used in room-and-pillar work, but not a great deal more. We have not attempted to recover much of our timber.

MEMBER.—Is the mine union or non-union?

GLENN B. SOUTHWARD.—Non-union.

HOWARD N. EAVENSON, Pittsburgh, Pa.—I went through that mine some weeks ago, and think that the author has been very conservative in his statements about the amount of loadings, etc.

EDWARD B. RAIGUEL, Huntington, W. Va. (written discussion).—The paper indicates that 60 men, employed in day and night shifts, inside the mine, produce 750 tons per day. Let us reduce these figures to a man-hour basis, for comparison with Mr. Eavenson's figures on West Virginia mines, as follows:

	MEN	HOURS		MAN-HOURS PER TON
Loading.....	32	8 = 256	or	0.340
Hoist operator.....	1	8 = 8	or	0.011
Cutting.....	4	8 = 32	or	0.043
Drilling and shooting.....	3	8 = 24	or	0.032
Timbering.....	12	8 = 96	or	0.128
Mechanical.....	6	8 = 48	or	0.064
Haulage.....	2	8 = 16	or	0.021
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Total inside.....	60	480	or	0.639
Outside.....	8	8 = 64	or	0.085
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Total inside and outside.....				0.724

Mr. Eavenson's figures are all on room-and-pillar mines and, therefore, show only the four standard subdivisions of labor.

The best single mine performance in West Virginia found in Mr. Eavenson's paper is as follows:

	MAN-HOURS PER TON
Loading. . . . .	0.39
Cutting. . . . .	0.04
Inside day labor . . . . .	0.30
Outside day labor . . . . .	0.12
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Total.....	0.85

These figures are on a non-union mine, where loaders drill and shoot, timber and clean coal, but do not extend track.

The foregoing figures show a difference in favor of Norton mine of 0.126 man-hours per ton, in spite of the fact that loaders in Norton mine spend over 30 per cent. of their time handling slate parting instead of coal. For purposes of comparison, let us assume that the Norton mine has 6 ft. of clean coal. The loader will, of course, load out the extra tonnage of coal in at least the same time that he loads out the present slate parting. The total daily tonnage will now be 1000 tons and the tabulation will show as follows:

	HOURS		MAN-HOURS PER TON
Loading.....	256	or	0.256
Hoist operator.....	8	or	0.008
Cutting.....	32	or	0.032
Drilling and shooting.....	24	or	0.024
Timbering.....	96	or	0.096
Mechanical.....	48	or	0.048
Haulage.....	16	or	0.016
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Total inside.....	480	or	0.480
Outside.....	64		0.064
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Total inside and outside.....			0.544

Now, for comparison with these figures, let us tabulate the best performance under each subheading as found in Mr. Eavenson's paper. This tabulation is as follows:

	MAN-HOURS PER TON
Loading.....	0 39
Cutting.....	0 02
Inside labor.....	0.30
Outside labor.....	0.08
Total .....	0.79

There is only a difference of 0.06 man-hour per ton between the best performance of a single mine and the total of the best performance in the four subheadings. In other words, if all these best performances were found in a single mine, the Norton mine would still show a difference of 0.246 man-hour per ton in its favor. I believe this to be a fair comparison, as all of Mr. Eavenson's figures are on mines with clean coal.\* I am also convinced that the figure for loading in 6 ft. of clean coal can be brought down to about 0.200 man-hour, which will be almost one-half the best performance recorded in room-and-pillar mines.

The probable roof action under heavy cover seems to be a point that frequently arises during a discussion of the V system of mining. This question is already answered by the present room-and-pillar system of mining. In practically all systems of robbing, except long-wall mining and modifications of same, the break line is run approximately in a direction of 45° from the entry. This leaves a series of steps across the panel which, when looked at from a point at right angles to the break line, resolve themselves into a series of V's with a 90° angle instead of a 45° angle. Now, if these faces stand with a 90° angle between the legs of the V, it is surely reasonable to suppose that a little longer face with only 45° angle will support the top. In fact, in the Pocahontas region in West Virginia, where rooms are driven on 80-ft. centers 20 ft. wide, the unsupported distance is 115 ft. as against 80 ft. in the V system, and still the robbing system is the same as in other room-and-pillar mines, although the cover varies from 300 to 900 feet.

MEMBER.—How does the roof stand in case of a shutdown?

GLENN B. SOUTHWARD.—We were shut down ten days over July 4, but as far as we could determine, there was no change in the roof during that time. There had been a fall, however, on July 2, the day before we shut down. We have found that the only time where a shutdown would probably be dangerous is just before a fall is to occur; in that case, unless the timbers were weakened so as to cause a fall, the weight would probably spread and cause a subsequent fall over a larger area than desired.

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\* See page 823.



MEMBER.—The mine runs three shifts?

GLENN B. SOUTHWARD.—Two shifts; that is one loading shift in the day and a night shift which does the cutting, timbering, drilling, shooting, and so on.

THOMAS DE VENNY, Edgerton, W. Va.—Mr. Raiguel compared the V system with the approximate face in the robbing and room-and-pillar system; in your system it is necessary to press your falls back from where they would be in the ordinary room-and-pillar system.

GLENN B. SOUTHWARD.—We try to break it right back behind the points. If the roof is strong or normal, we generally have the break pretty close to the points.

THOMAS DE VENNY.—The comparison was not exactly the same, as I saw it. In the room-and-pillar system, it is not necessary to make any attempt to break the roof back of the edge of the pillar, the pillar itself breaks it.

GLENN B. SOUTHWARD.—In the V system, the slate immediately over the coal is supported on timbers in the angle or V while the overlying sandstone bridges, or spans, across this space and is supported by the coal along the faces and in the points. Because of this bridging effect, we do not have the severe weight due to the overlying measures back in the angle where the sandstone is strong enough to span this distance. Out beyond the points, the mined area is large enough for the sandstone to either break or subside and this in turn relieves the weight and prevents a squeeze, or creep. Without discussing any roof theory, we feel sure that this is what happens because we do not have severe weight back in the angle; and from observations on the surface we know that the sandstone out beyond the points either breaks or subsides.

Mr. Raiguel's point was that if it is possible to get complete breaks in a room-and-pillar system, where generally 50 per cent. of the coal is removed and the remaining pillars are strong enough to break the top, better roof results could be expected in the V system where there is a much higher percentage of coal unmined at the time the falls occur.

J. J. RUTLEDGE,\* Baltimore, Md. (written discussion).—It seems strange that mining men will continue to use the old methods when newer and more improved methods will give not only greater recovery but a material reduction in the cost of brushing and of yardage. This fact is shown in Fig. 3 as the amount of narrow work necessary in the left-hand portion of the cut is much less than that in the right-hand.

Some miners say that they would willingly mine exhaustively, using improved methods, if they could be assured of freedom from claims for

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\* Chief Mine Engineer, Maryland Bureau of Mines.

damages due to subsidence of the surface. While this is a great obstacle to introducing improved mining methods in those parts of the country where the surface is of great value, the objection does not prevail in many other coal fields, where the surface is much less valuable. For example, in some portions of Oklahoma, the surface land was sold at an average price of \$12 per acre while the prevailing royalty returns under present methods of mining, yield about \$300 per acre. It is much better business to sacrifice the \$12 value of the surface than to waste 50 per cent. of the valuable coal.

The summary shows that the output per man employed is much higher than that realized under ordinary room-and-pillar methods and that the cost of producing coal is correspondingly lower; this has been my experience in trying out panel long wall. The author also shows that a considerable output is obtained from a very small area and that mining costs are reduced proportionately. His concluding paragraph cites experiences that have a parallel in other fields where panel long-wall mining has been tried.

Under these new methods of mining where men work together, and are not working singly, as they are in many room-and-pillar mines, there is a much better feeling of security and the *esprit de corps* is much better than in the other mines. In the old advancing long-wall methods employed in northern Illinois, the miners met each other at the end of their "marches" and there was always a certain amount of companionship extending clear around the long-wall face. It is time mining men began to consider the psychology of mining as well as the engineering and economic features of it. Mr. Southward and Mr. Drennan are to be congratulated on the results achieved; certainly the carrying out of such a plan required the exercise of considerable courage.

GRAHAM BRIGHT, Pittsburgh, Pa. (written discussion).—I have had the privilege of witnessing the operation of the Movor conveyor as applied to the V system of mining, and am much impressed with its possibilities not only as applied to the V system, but to the regular room-and-pillar system, as well. The heavy parting at the Norton mine of the West Virginia Coal & Coke Co., which must be handled separately, makes the application of a mechanical loader rather difficult. Where there is no parting, a loader may show considerable additional saving.

One of the principal drawbacks to the mechanical loader is that it can be kept working only a comparatively small part of the time, because of the difficulty of keeping it supplied with empty cars. With a conveyor system, there is no reason why the loader could not work continuously until the place is cleaned up.

The speed of 50 ft. per min. for the conveyor on the working face is very moderate, and even the cross-entry conveyors, which operate at

about 100 ft. per min., have a very moderate speed. The main lateral conveyor, however, would have to operate at 400 ft. per min., if all cross conveyors were loaded, which might be the case early in the shift.

I believe that the author expects to get around this difficulty by making the lateral conveyor wider. I would suggest substituting a belt conveyor for the pan type in the lateral entry. The belt conveyor can be run faster than a pan conveyor, requires considerably less power, and the first cost may be less. This main conveyor is generally fixed in length so that there would be no particular objection in making it a belt type. The belt conveyor, could, however, be designed in sections, so that it could be readily lengthened or shortened. I believe that a belt conveyor would require less than one-half the power taken by a pan conveyor.

In a long conveyor mine, where the main conveyor to the tippie may be 2000 or 3000 ft. long, and of fairly high capacity, it would seem that the belt conveyor might have some decided advantages over the pan type. The pan type would require a drive unit approximately every 50 ft. The belt-type conveyor can have the drive units very widely separated; belt conveyors have been installed with the drive units 2000 ft. apart. As the first cost of these drive units is rather high, this should represent a considerable saving in a long conveyor, both from the first cost standpoint and the standpoint of power consumption.

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## Timber Used in Bituminous-coal Mining

By NEWELL G. ALFORD, PITTSBURGH, PA.

(New York Meeting, February, 1924)

FORECASTS of future timber consumption in soft-coal mining are handicapped by the lack of adequate experience records for estimating properly the timber requirements of the industry.

Data were obtained from plants where records are kept or from operators who collected the information and to these were added

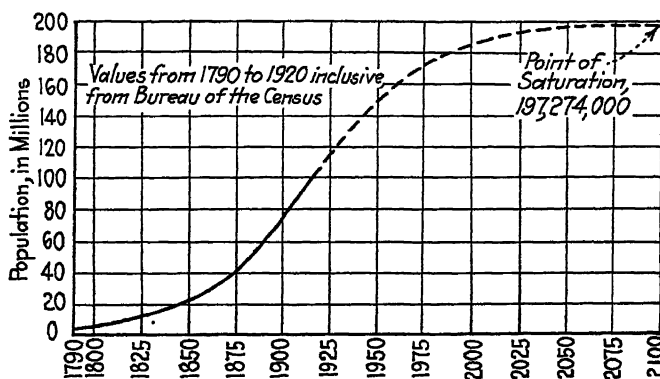


FIG. 1.—GROWTH OF POPULATION IN UNITED STATES, FROM PEARL'S "BIOLOGY OF DEATH."

composite figures for the continental United States in 1905 and 1919<sup>1</sup> and for central and western Pennsylvania and for Illinois in 1922.<sup>2</sup> The result, representing slightly over 928,000,000 net tons, is shown in Table 1. Some of the companies furnishing data were unable to segregate the timber into classes of use but for those who did, Table 2 shows the board feet of posts and cross bars used per ton of coal mined and the percentage of the total timber consumed that was used in roof support. The wide variation in amounts of timber per ton of coal mined is the result of

<sup>1</sup> Forest Service Circular 49, U. S. Dept. of Agriculture (Timber used).

<sup>2</sup> Reports of Investigations, Bureau of Mines, Serial Nos. 2465 and 2546 (April and November, 1923).

TABLE 1.—*Timber Used in Bituminous Coal Mining*

State	District	Seam	Net Tons Mined	Board Feet Timber Used	Board Feet Timber Used per Net Ton Coal Mined	Remarks
Pennsylvania.....	Connellsville	Pittsburgh Upper & Lower Kittanning	17,004,513	74,415,317	4.36	One year's figures (1923).
Pennsylvania.....	Somerset Co.	Georges Creek	977,814	5,998,919	6.13	One year's figures.
Maryland.....	Frostburg	Pittsburgh	237,709	929,232	3.91	One year's figures.
West Virginia.....	Fairmont	Pittsburgh	55,375	191,332	3.45	Figures for one representative month.
West Virginia.....	Fairmont	Eagle	81,431	120,932	1.50	Figures for two representative months.
West Virginia.....	Paint Creek	Poosahontas	102,512	847,901	5.22	Figures for 10 months.
West Virginia.....	Tug River	Winfrede	25,205,829	81,871,705	3.25	Figures for 7 years.
West Virginia.....	Thacker	Millers Creek	517,013	850,623	1.64	Figures for 2 years.
Kentucky.....	Big Sandy	Elkhorn	137,769	897,342	6.51	Figures for 1 year.
Kentucky.....	Big Sandy	No. 9	1,469,596	9,420,423	5.67	Figures for 1 year.
Kentucky.....	Western	All	132,000	227,040	1.72	Figures for 3 months.
Illinois, 1922.....	All	All	22,000,000	60,720,000	2.76	Figures for 1 year, from 30 operators.
Colorado.....	"	Nine Seams	3,175,000		0.35	Serial 2465, Bureau of Mines.
New Mexico.....	Raton	Three Seams	609,176	4,041,321	6.63	Figures for 1 year.
Illinois.....	"	No. 6	2,319,000	3,826,350	1.65	Figures for 9 months.
Pennsylvania, 1922.....	Cent. & West.	All	37,000,000	133,200,000	3.60	Figures for 1 year (1921).
United States, 1919.....	All	All	465,860,058	1,813,630,000	3.89	Serial 2546, Bureau of Mines, 1923 Consumption in 1919.
United States, 1905.....	All	All	351,062,785	1,236,506,400	3.52	R. R. Hornor, Bureau of Mines. U. S. Forest Service Cir. 49. Dept. of Agriculture.
Total above.....			928,067,600	3,447,915,119	3.71	Weighted average per ton.

\* In Las Animas, Huerfano and Fremont Counties.

None of the figures given for total states or the United States duplicate those of individual companies.

differing mining conditions and variance in the quality and strength of the timber.

Fig. 1 shows the past and estimated future population of the continental United States to the probable saturation point in 2100 A.D. Fig. 3 gives the past and estimated future total fuel consumption, including oil and gas, taken from Fig. 2, and while the latter curve largely explains why the production of bituminous coal has not been increasing in the past five years it also shows that the period of peak oil production is passing and that, after 1925, a progressive recession is expected. The total coal and the bituminous-coal curves for expected production, Fig. 3,

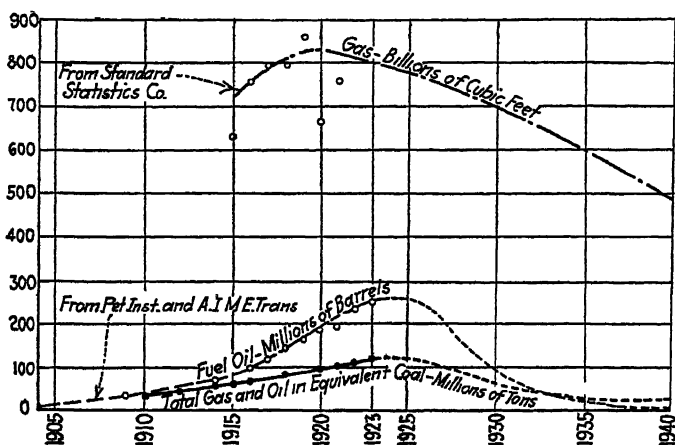


FIG. 2.—PAST AND ESTIMATED FUTURE OIL AND GAS PRODUCTION OF UNITED STATES AND TOTAL EQUIVALENT IN COAL.

take into account the future recessions in the railroad and industrial use of oil as the supply is curtailed and the consequent increase in demand for coal as oil prices advance.

Oil production processes are developed that can triple the extraction of gasoline from fuel oil at relatively small increased cost to refiners, only the added cost preventing their present use; the supply of available fuel oil will diminish with the certain enormous increase in the use of gasoline by automobiles. While the shallower fields near exhaustion, the cost of sinking and operating deeper wells will increase and sooner or later the United States Navy will discount its future need for conservation of fuel oil and secure legislation restricting its use to government purposes. With these factors affecting oil production and consumption, it is believed the demand for coal and its consequent increased production, due to the diminished supply and higher price of oil, will rise at least as rapidly as it declined.

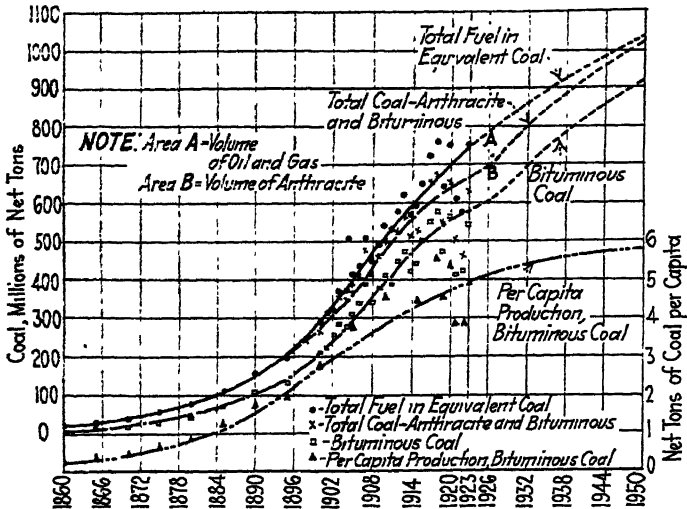


FIG. 3.—PAST AND FUTURE TOTAL FUEL, TOTAL OF ANTHRACITE AND BITUMINOUS COAL, BITUMINOUS COAL PRODUCTION, WITH PAST AND FUTURE BITUMINOUS COAL PRODUCTION PER CAPITA IN THE UNITED STATES; ACCORDING TO DATA OBTAINED FROM THE U. S. GEOLOGICAL SURVEY, AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS, AMERICAN PETROLEUM INSTITUTE.

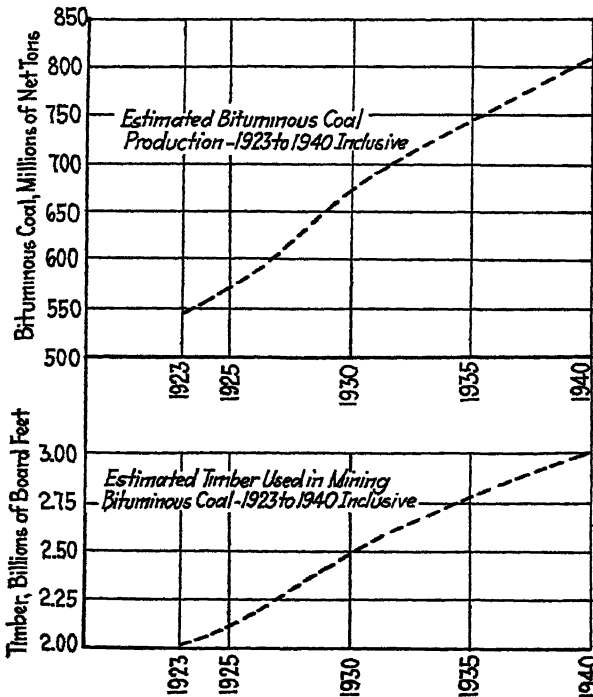


FIG. 4.

Increased efficiency in making electric power and its wider and more efficient application will restrain to an extent the production of coal per capita, as shown in Fig. 3, with the expected stabilizing of this unit taking effect in a decade or so after 1950.

Fig. 4 gives the expected trend of bituminous-coal production from 1923 to 1940, as based on data developed in Fig. 3 and, using the unit of 3.71 board feet of timber per ton of bituminous coal mined, shows the consequent growth in the use of timber for the same period in soft-coal

TABLE 2.—*Timber Used for Posts and Cross Bars*

State	District	Seam	Board Feet per Net Ton Coal	Per Cent. Total Timber Used
West Virginia.....	Tug River	Pocahontas	2 44	75.6
West Virginia.....	Thacker	Winifrede	3 38	20.6
West Virginia....	Paint Creek	Eagle	4.09	78.8
Maryland.....	Frostburg	Georges Creek	2 68	68 6
Pennsylvania. ....	Somerset Co.	Upper & Lower Kittanning	5.06	82.8
Kentucky.....	Big Sandy	Elkhorn	4 56	71.1
Kentucky.....	Big Sandy	Millers Creek	5 60	55.4
Kentucky....	Western	No. 9	0 71	41.8
New Mexico .....	Raton	Three Seams	6 35	90 6

mining, but it is expected that the true average timber consumption per ton of coal will be slightly higher rather than under this weighted average. The values determined by the expected timber consumption curve in Fig. 4 are tabulated in Table 3.

TABLE 3.—*Estimated 1923 and Future Timber Consumption in Bituminous-coal Mining*

	BOARD FEET		BOARD FEET		BOARD FEET
1923.....	2,021,950,000	1929.....	2,415,000,000	1935.....	2,756,530,000
1924.....	2,062,760,000	1930.....	2,485,700,000	1936.....	2,814,000,000
1925.....	2,114,700,000	1931.....	2,547,000,000	1937.....	2,860,000,000
1926.....	2,175,000,000	1932.....	2,609,000,000	1938.....	2,910,000,000
1927.....	2,226,000,000	1933.....	2,662,500,000	1939.....	2,956,000,000
1928 .....	2,330,000,000	1934.....	2,708,000,000	1940.....	3,005,100,000

The data from which the shown results are obtained are from thoroughly reliable sources and, so far as is known, are the most complete yet compiled.



## Valuation of Coal Mining Properties in the United States

### REPORT OF THE ENGINEERS' ADVISORY VALUATION COMMITTEE OF THE UNITED STATES COAL COMMISSION\*

(New York Meeting, February, 1924)

THE COMMITTEE, appointed early in May, met and organized in Washington, May 9, 1923, and were then advised that such data as they required would as far as obtainable be submitted to them in tabulations, and that they could not be allowed to see the individual reports nor know the identity of the operators on whose reports the figures submitted were based, therefore the Committee's valuation is based on data received from your statisticians, and on tonnages estimated by your staff and by the United States Geological Survey.

Various methods of valuation for mining properties have been suggested, but all authorities seem to agree in accepting, as the fairest and most practicable and logical, a capitalization of the estimated future earnings, when such estimate can reasonably be made. Hoover and Finlay both emphasize this.

The United States Supreme Court says in *Cleveland, Cincinnati, Chicago & St. Louis Railway Co., v. Backus*, 154 U. S. 439:

But the value of the property results from the use to which it is put and varies with the profitableness of that use, present and prospective, actual and anticipated. There is no pecuniary value outside of that which results from such use. The amount and profitable character of such use determines the value.

The Committee on Federal Taxation of the American Institute of Mining and Metallurgical Engineers, appointed in 1919, in its report states:

A proper value of a mining property is the present value of the prospective net earnings, taking into account probable variations in output and value.

Ingalls ("Wealth and Income of the American People," p. 97) says:

The fundamental principle of mine valuation is the present worth of an annual dividend accruing during the period of years corresponding with the life of the mine. It is a convention that the estimated period shall not be more than 30 years.

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\* This report was submitted to the United States Coal Commission, and the Committee was advised that it would be submitted to Congress but would not be made public with the reports of the Commission. The Commission, however, gave its permission for publication by the Committee.

Other methods of valuation are: Cost values; Assessed valuation; Sale values; Royalty valuations, Tonnage values and the like.

*Cost*, which is urged as representing the actual investment in a property, is no criterion of value; the great bulk of the anthracite lands were patented to individuals by the State of Pennsylvania from about 1795 to 1816, at from two to four dollars per acre. No one could consider that as a present value, and if it were maintained the anthracite communities would be bankrupt for lack of taxable assets, yet \$4 per acre at 6 per cent. compound interest from 1800 to date would amount to \$5200 per acre, more than the present average value of the lands, and the undeveloped area has paid taxes for all this time, besides accumulating interest.

If the last purchase price be taken, the wildest confusion and injustice ensues, a property which may have cost \$1000 a half century ago would be valued at that in the hands of the original purchasers, on its sale it may immediately jump to \$100,000 in the hands of a new owner, while identical property not sold remains valued at the original cost.

*Assessed valuation* is not a reliable indication of value, particularly in the case of coal where the widest variation exists in the values assigned in adjoining counties and municipalities, and when quite generally coal land in the hands of the farmers is unassessed or assessed at nominal value. Similar land in the hands of operating companies, even if undeveloped, is often heavily assessed. In the anthracite region, the basis of valuation varies from about \$30 to \$500 per foot-acre for land in adjacent counties.

*Sale prices* are a just basis of valuation for the *particular lands sold*, provided that the sale was between a "willing seller and a willing buyer," but sales are not even an indication of the value of other properties. As is well known, one mine may be a bonanza and the adjoining one a liability. Further, the value of a mining property may be greatly enhanced, or much depreciated, by the method adopted in opening, development or equipment; and in the sale of properties all of these considerations are taken into account.

*Royalty values* are useful as indications of value of unopened lands, it is self-evident that any one paying royalty expects to make a material profit above that royalty, and the value of operating lands is hence based on the sum of the royalty to the lessor and the profit to the lessee.

*Tonnage Values.*—While all values can be reduced to value per ton, there is a tendency to estimate tonnage and then apply an assumed figure of value per ton; this is not a valuation but guessing.

After a full consideration of all the above methods your Committee, in fixing a general value of coal lands, has used as far as practicable the present value method for operating properties, considered as covering the "available coal" being the probable future output for 40 years; all coal in

any district not included in the 40-year output is classed as reserves and the method of its appraisal is hereinafter explained.

*Data.*—We requested, from data collected by the United States Coal Commission, Federal Trade Commission, and by the United States Geological Survey, statements of tonnage by years to date; days worked, operating cost (with royalty, depletion, depreciation, interest, and Federal taxes separate) returns from sales, and tonnage remaining, all bituminous coal divided into fields in accordance with the U. S. C. C. fielding map, and anthracite into four fields, northern, eastern middle, western middle, and southern.

*Basis of Valuation.*—The weighted average of data for the years 1920 and 1921, where such is available, was used as a base: first, because this was believed to fairly represent present conditions; second, any changes of conditions in costs would, we believe, be reflected in the realization; third, the data in the possession of the Commission is most complete for these years. Where the 1920–21 earnings were unavailable or misleading, the most reliable available data were used.

As the total value of the properties is desired, costs are figured before royalty, depletion, depreciation, and interest charges; royalty in the case of leased and depletion in the case of fee lands represents the value of the undeveloped coal in the ground, depreciation the value of improvements and developments, and interest charges and profits the returns to capital used in operation. Federal taxes are a charge against income and must be deducted from the realization before it can properly be used in estimates of value.

*Future tonnage* is estimated from consideration of past tonnage and of reserves in each district; Figs. 1 to 5.

*Value of Operating Property.*—From the above, the value of the operating properties is determined by discounting at 6 per cent. compound interest the net yearly returns, as a varying annuity estimated for each field for the period noted, obtained by applying the values as above indicated per ton to the estimated tonnage for each year.

*Value of Reserves.*—The reserve tonnage is determined by the difference between the operating tonnage as above and the total estimated tonnage in each field, this is considered as a whole in each field as undeveloped coal, the value of this is based on either actual sales of virgin areas where such sales of recent date are available and sufficient to justify their general employment in the estimates, or lacking that on the present value of the reserve coal at the present rates of royalty, but considered deferred for the life of the operating lands.

*Total Valuation.*—Based on the above, the total valuation is made up of the value of operating coal land and reserves, and includes development and equipment, as well as all land values, regardless of whether the ownership is in the operating company or the lands operated under lease.

## ANTHRACITE VALUATION

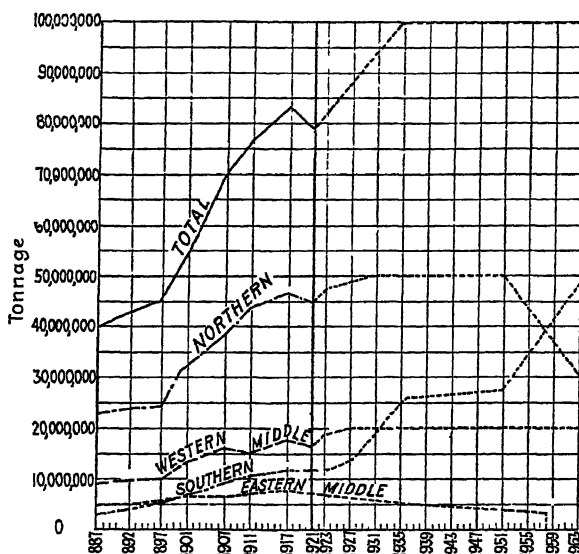


FIG 1 —PAST AND ESTIMATED FUTURE TONNAGE, BY FIELDS, OF ANTHRACITE REGION, PENNSYLVANIA.

Reasonably complete data, as requested, were furnished by your statisticians, together with the Commission's estimate of coal.

FIELD	TOTAL COAL RE- MAINING	PER CENT. RECOV- ERABLE	RECOVERABLE COAL REMAINING
Northern.....	3,276,763,000	67.0	2,195,431,000
Eastern Middle.....	248,628,000	69.4	172,548,000
Western Middle.....	3,573,025,000	58.1	2,075,928,000
Southern.....	9,256,260,000	49.0	4,535,567,000
Total.....	16,354,676,000		8,979,474,000

From a study of past production, we estimate as a conservative basis of value that the field as a whole can increase by 1935 to about 100,000,000 gross tons per year, and hold this average production to the end of the 40-year period allowed for available coal, as shown on attached diagram.

The reserves, mostly in the western middle and southern fields, are expected to hold the 100,000,000 tons output for about 10 years longer and then gradually decrease to 50,000,000 tons per year with a total life of about 70 years additional.

As important factors in production, we estimate for the northern field a life of 50 years; for the eastern middle, 35 years; the western middle, 100; and the southern field, 110 years. All of these fields will, of course, produce coal long after the above limits, but in small quantities and of negligible present value.

The western middle and southern fields will have to carry on after the other two fields cease to be important factors, owing to depth and to geological conditions, resulting in a much smaller percentage of domestic sizes, the coal from these fields is more costly to mine and brings less realization all sizes; hence these fields are naturally only developed to carry the surplus demanded by the market over that furnished by the cheaper northern and eastern middle fields; but these more costly fields have the greatest reserves and can be expected to maintain a large production long after the more favored fields are exhausted.

The average royalty paid on all coal sold was found to be 16.5 cents per ton, the average depletion 14.7 cents, and average depreciation charged on plant 10.8 cents.

Valuing the available coal, plant, and improvements on the basis of the returns found from the Commission's figures, discounted to the present time, and the reserves on probable margins deferred 40 years, we estimate the present value of the properties comprising the Pennsylvania anthracite field as follows:

Available recoverable tonnage.....	3,907,900,000
Reserves recoverable tonnage.....	5,071,600,000
<b>Total recoverable tonnage.....</b>	<b>8,979,500,000</b>
Present value of plant, improvements, and available tonnage.....	\$843,500,000
Present value reserve tonnage.....	146,400,000
<b>Total present value.....</b>	<b>\$989,900,000</b>

#### BITUMINOUS VALUATION

In appraising bituminous coal, your Committee, in addition to considering recent earnings submitted, has given full consideration to all data available, earnings of earlier years, sales values, royalty rates, and past performances, and presents hereinafter estimates of tonnage and value which it believes to be most conservative and fully justified by the data obtained.

The *total tonnage* is based on estimates of the U. S. Geological Survey, and of various state surveys, all revised and reduced to allow for losses in mining and for thin and unavailable coal included in these estimates but not considered as of special value. The total tonnages considered in the Committee's estimate are actually materially less than one-half of the tonnage estimated by the U. S. Geological Survey as remaining at the end of 1920.

*Available coal* is estimated as that commercially mineable within 40 years, allowing for probable gradual increases in the rate of output

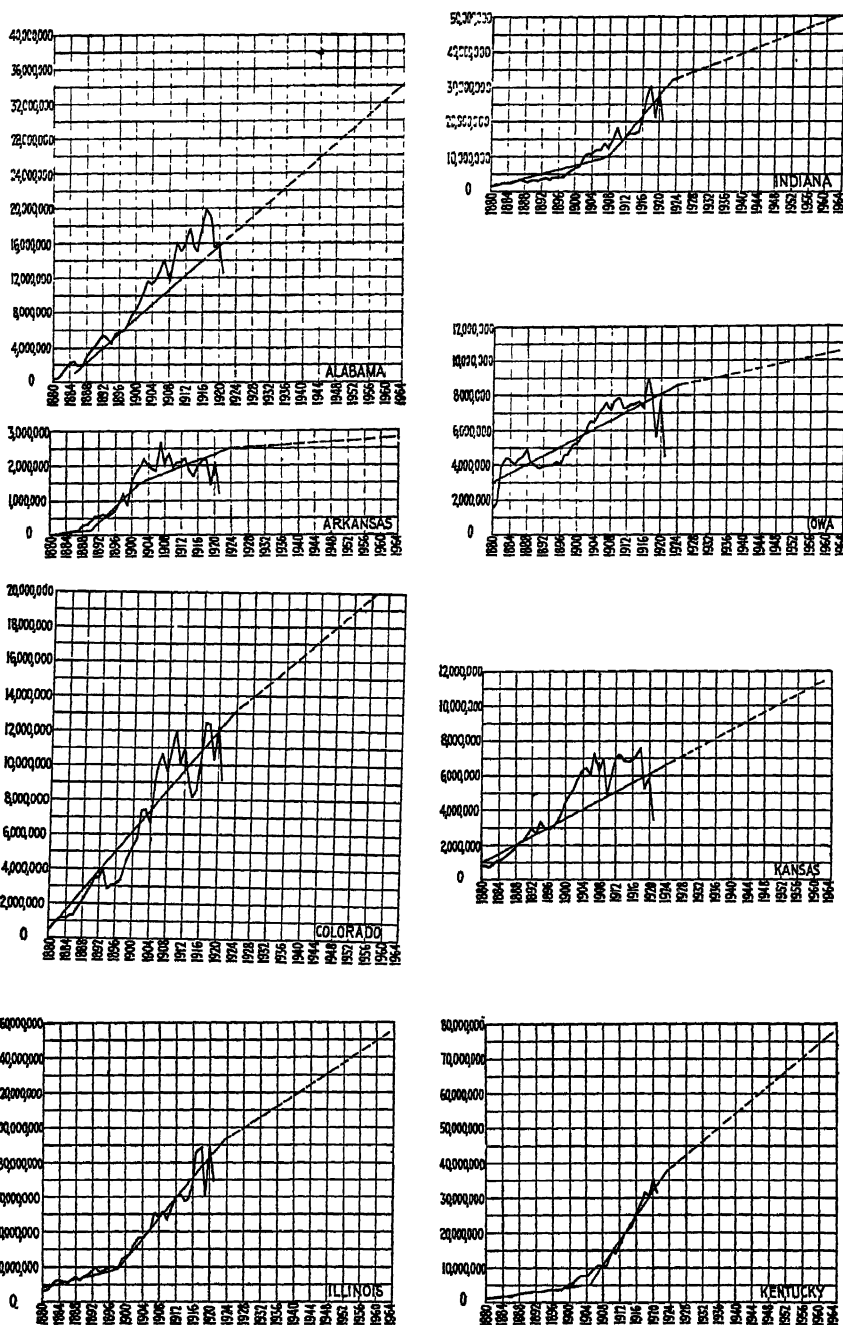


FIG. 2.—PAST AND ESTIMATED FUTURE PRODUCTION OF BITUMINOUS COAL, BY STATES.

# 800 VALUATION OF COAL MINING PROPERTIES IN THE UNITED STATES

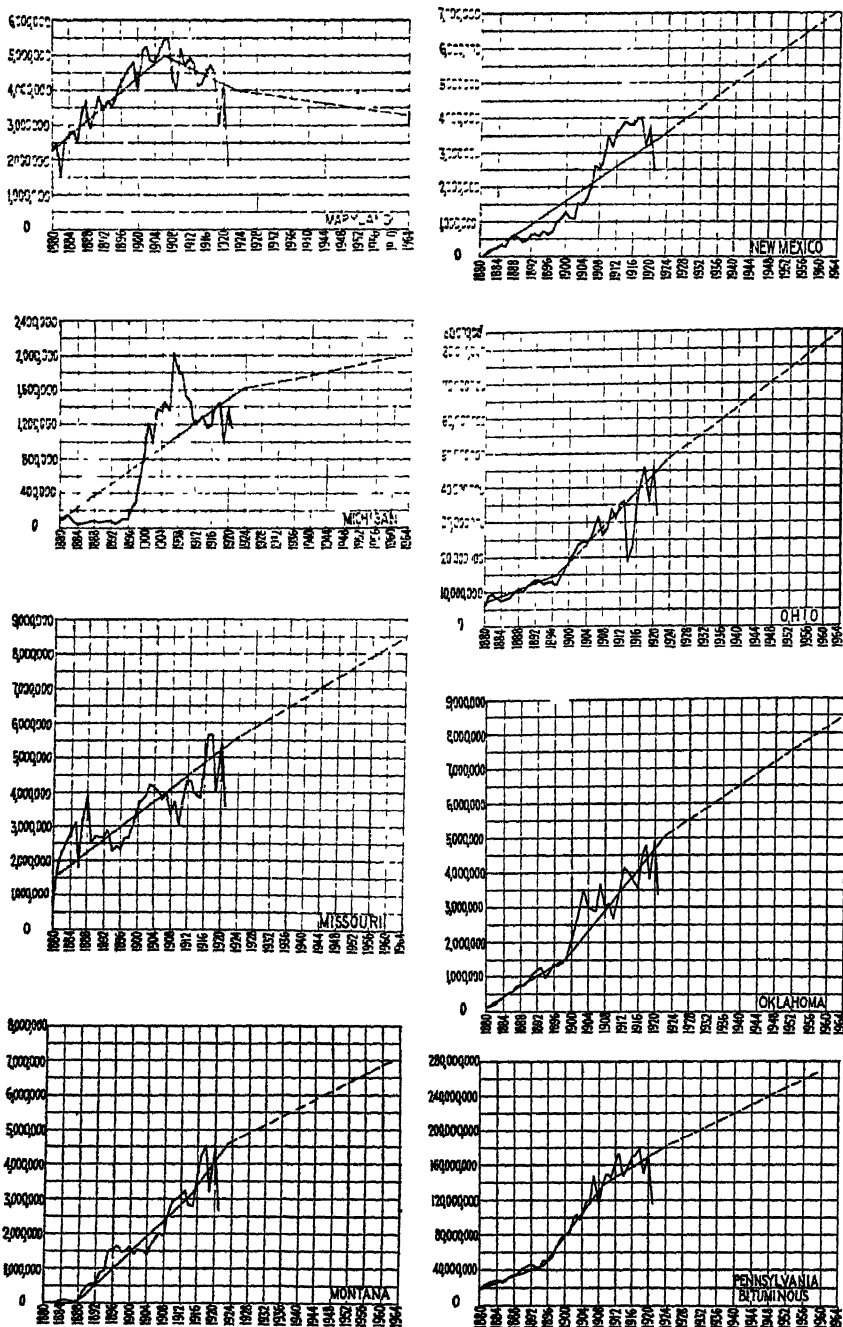


FIG. 3.—PAST AND ESTIMATED FUTURE PRODUCTION OF BITUMINOUS COAL, BY STATES.

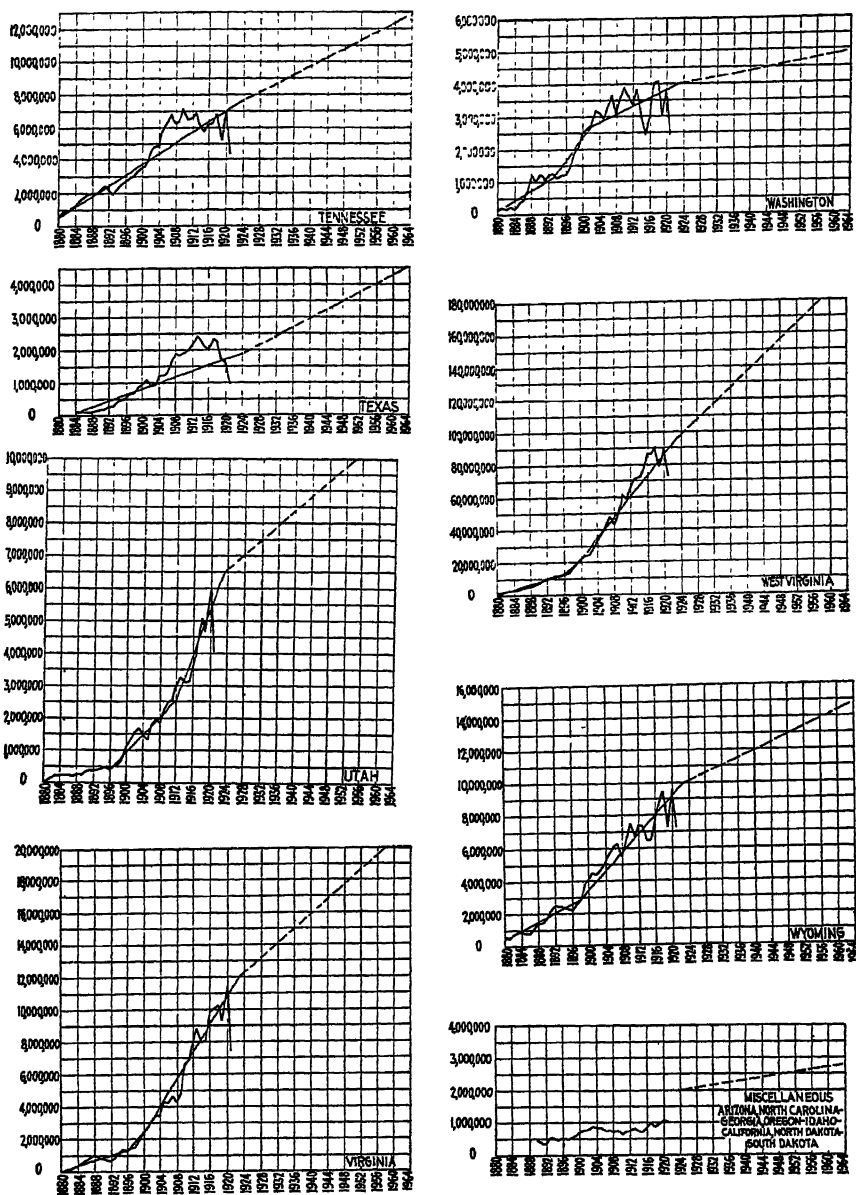


FIG. 4.—PAST AND ESTIMATED FUTURE PRODUCTION OF BITUMINOUS COAL, BY STATES.



to a total for the whole industry of 1,000,000,000 tons per year at the close of the 40-year period.

*Reserves* are considered as such coal as would be available after the exhaustion of the available coal, excluding from any consideration all coal so situated as to be impracticable of access, and all coal so thin or of such depth as to have no present sale value.

In determining the amount of reserve coal, an effort has been made to confine this item to coal which at the present time, or at least within the 40-year life of the available coal, would have actual ascertainable sale value, and be capable of beneficiation.

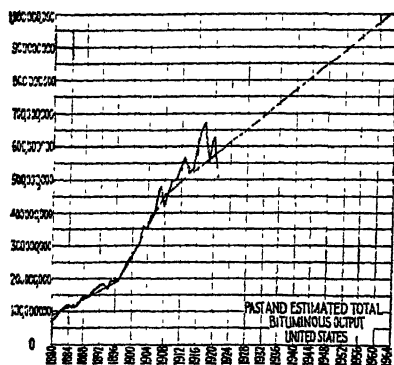


FIG. 5.—PAST AND ESTIMATED FUTURE PRODUCTION OF BITUMINOUS COAL—TOTAL FOR UNITED STATES EXCLUDING ALASKA.

As the values of available coal were obtained by discounting probable earnings, these values necessarily include all plant, development, equipment, mine housing, and other properties directly connected with the business. They do not include outside factors as interest or rentals received, profits from connected undertakings as stores, farms, selling of purchased coal and the like. The values of reserves are those of the coal land only and are, in general, far below the market price of similar lands in the same localities. It is the feeling of your Committee that all the coal to be mined within 40 years, whether from present or future operations, is included in available coal and that all reserve values should be treated as deferred.

The Committee's estimate of the value of the coal properties of the country, not including coal in Alaska or in the island dependencies of the United States, is as shown in Table 1.

The value of the available tonnage \$7,129,714,000, is the minimum on which earnings should be based. Considerable amounts of reserve tonnage are, and should be, held by operators to protect their future interests, and earnings must be sufficient to cover the carrying of reasonable holdings of such reserves.

TABLE 1.—*Estimate of Present Value of Coal Lands, Plant and Improvements, in the United States*

State	Tonnage		Available Tonnage Including Plant and Improvements	Reserve Tonnage	Total
	Available for Mining within 40 Years, Tons	Reserves of Present Value after 40 Years, Tons			
Alabama.....	1,020,000,000	32,000,000,000	\$ 130,560,000	\$ 162,000,000	\$ 292,560,000
Arkansas.....	106,000,000	860,000,000	22,048,000	21,500,000	43,548,000
Colorado.....	680,000,000	157,000,000,000	144,180,000	157,000,000	301,180,000
Illinois.....	4,920,000,000	49,000,000,000	984,000,000	490,000,000	1,474,000,000
Indiana.....	1,640,000,000	25,000,000,000	229,600,000	125,000,000	354,600,000
Iowa.....	380,000,000	14,000,000,000	30,400,000	14,000,000	44,400,000
Kansas.....	354,000,000	14,000,000,000	49,560,000	14,000,000	63,560,000
Kentucky.....	2,290,000,000	60,000,000,000	421,360,000	600,000,000	1,021,360,000
Maryland.....	144,000,000	160,000,000	37,440,000	8,000,000	45,440,000
Michigan.....	72,000,000	30,000,000	11,520,000	900,000	12,420,000
Missouri.....	278,000,000	20,000,000,000	33,360,000	20,000,000	53,360,000
Montana					
Bituminous } ...	232,000,000	1,500,000,000	33,408,000	98,250,000	131,658,000
Lignite		181,500,000,000			
New Mexico					
Bituminous } ...	210,000,000	9,000,000,000	47,670,000	88,000,000	135,670,000
Sub-bituminous		86,000,000,000			
Ohio.....	2,640,000,000	32,000,000,000	485,760,000	640,000,000	1,125,760,000
Oklahoma.....	270,000,000	18,000,000,000	37,800,000	90,000,000	127,800,000
Pennsylvania.....	8,920,000,000	26,000,000,000	1,998,080,000	780,000,000	2,778,080,000
Tennessee.....	402,000,000	8,000,000,000	70,752,000	20,000,000	90,752,000
Texas					
Bituminous } ..	124,000,000	2,000,000,000	7,440,000	11,000,000	18,440,000
Lignite		12,000,000,000			
Utah.....	350,000,000	46,000,000,000	64,400,000	230,000,000	294,400,000
Virginia					
Anthracite } ....	660,000,000	100,000,000	132,000,000	201,000,000	333,000,000
Bituminous		10,000,000,000			
Washington.....	178,000,000	32,000,000,000	35,600,000	80,000,000	115,600,000
West Virginia.....	5,540,000,000	61,000,000,000	1,196,640,000	915,000,000	2,111,640,000
Wyoming					
Bituminous } ...	494,000,000	40,000,000,000	71,136,000	350,000,000	421,136,000
Sub-bituminous		300,000,000,000			
Miscellaneous*					
Bituminous } ...	96,000,000	2,000,000,000	11,520,000	41,000,000	52,520,000
Sub-bituminous		4,000,000,000			
Lignite		350,000,000,000			
Total, excluding lignite.....		1,049,650,000,000			
Total lignite.....		543,500,000,000			
Total.....	32,000,000,000	1,593,150,000,000	\$6,286,214,000	\$5,156,650,000	\$11,442,864,000
Pennsylvania, anthracite.....	3,907,900,000	5,071,600,000	843,500,000	146,400,000	989,900,000
Grand total....	35,907,900,000	1,598,221,600,000	\$7,129,714,000	\$5,303,050,000	\$12,432,764,000

\* Miscellaneous includes: Arizona, California, Georgia, Idaho, North Carolina, North Dakota, Oregon, South Dakota.

*Plant.*—The data presented are not sufficient to permit the determination of the actual value of plant and equipment, nor do we believe that such data could be obtained of sufficient accuracy to warrant their general application. The total value of plant and equipment in the bituminous fields varies from \$1 to about \$3, and in the anthracite region of Pennsylvania, from \$1.50 to as high as \$4.50 per ton of annual output. Employee housing, of good type, costs, under present conditions, upwards from \$1 per annual ton.

Your Committee has endeavored to be distinctly conservative in estimating both tonnages and values, and collectively and separately desires to express most forcefully the opinion that the properties valued either as available or reserve could not be purchased in the open market except at a price far beyond the Committee's estimates.

The discount rate used, 6 per cent. for anthracite and 8 per cent. for bituminous, are those adopted by the U. S. Treasury Department for the income tax valuations.

In conclusion, careful studies have been made in detail of regions and districts, in both the anthracite and the bituminous valuations. With the limited time available it is impossible to present these in such form as to be informative to the public, and your Committee therefore confines its report to the general methods used and to the results reached.

Very truly,

*September 19, 1923.*

R. V. NORRIS,  
SAM'L. A. TAYLOR,  
HOWARD N. EAVENSON,  
H. M. CHANCE,  
JAS. H. ALLPORT, *Committee.*

## Data about Labor Employed in Various Bituminous Coal Mines

By HOWARD N. EAVENSON, PITTSBURGH, PA.

(New York Meeting, February, 1924)

THE information contained in the following paper was collected at the request of the U. S. Coal Commission, and is published with the permission of that body and of the various companies furnishing the data. For obvious reasons, the names of the companies are not given. No data were obtained from states south of Virginia or west of the Mississippi River.

The data about the amount of labor, in man-hours, required in producing a ton of bituminous coal have been collected with the idea of showing what is being done at some well-managed plants, and not to show the average amount required by all mines, which undoubtedly is considerably higher than the average of the figures shown.\* Almost all of the figures were supplied by the various companies in reply to a questionnaire; when they were obtained from other sources the company was asked to verify them. On account of the amount of work required, the data were only requested for one or two months for each plant, and the figures represent in each case a month when the car supply was good and the work was practically steady. In the case of most of the West Virginia and Kentucky mines, these conditions were best met in May and June, 1922.

The mines for which the figures are given are arranged by states and as to whether the mine operates under union or non-union or open-shop conditions. The union mines listed are generally considered to be as well-managed as are the non-union ones.

The production per month in a few cases includes the amount of slate which is loaded and hauled out of the mine, as of course this requires nearly as much labor per ton as does the coal. These cases are noted.

The number of days worked includes only the total time in which the tippie operated; not the number of days on which the mines operated. This makes the output per day appear slightly higher than it should be in

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\* The average figures for year 1921 have been computed from reports of U. S. Coal Commission and added to these tables.

these cases, but does not affect the item of "days worked," as the total days worked per month for each class, or the average number of each class working per day, were reported. It is hardly likely that any error introduced by this factor will be as great as the variation in production is from month to month, even at the same plant.

The number of machine men working per day includes both machine runners and helpers and, in computing the average production per day, the crew of two men is used as the divisor and the number of man-hours per ton includes the time of both men. The coal produced per machine sometimes includes *all* coal produced, both pick and machine, as data were not always available for separating this; in all cases where it could be separated, it is shown and computed separately. The number of man-hours per ton is computed from the actual number of hours in the working day at each plant and not from the time actually spent at the face. As a usual thing, the loader does not spend the total working time at the face; and in most mines, the actual time at the face does not average over about seven hours. All labor required in producing coal is included in the figures, whether employed inside or outside.

The figure in the column headed "Greatest tonnage loaded in one day" is the largest amount loaded during that month; in the next column are given the answers to the inquiry whether the loaders could average more if a full car supply was available.

In the accompanying tables, the figures under total labor are not the sums of figures in the previous columns; each item is the minimum or maximum of the figures in its class. For all of the mines given the data can be summarized as shown in Table 1.

The production per loader in mines Nos. 9 and 27 is the average production of thousands of men in different states and in many mines under different conditions. There is no doubt that this rate can be equalled in nearly all mines with approximately the same coal thicknesses and it should be excelled in many mines with better roof conditions.

In comparing the amounts of day labor required in the Illinois, Indiana, and Ohio mines with those in Eastern Kentucky, West Virginia, and Pennsylvania, it must be considered that pillar withdrawal is practically unknown in the former three states, while largely practiced in the latter ones.

Estimates show that in the latter mines the amount of inside day labor could be reduced from 25 to 50 per cent., which would affect not only the slate, timber, and track-men, but the men engaged in transportation, if the same methods of mining were practiced. This increase in day labor required for pillar withdrawal is, of course, balanced against the increased yield of coal per acre.

If all of the best performances could be grouped at one plant, it would be possible, by present methods, to produce a ton of coal with an amount

TABLE 1.—*Summary*  
Man-hours Required per Net Ton

	Loading	Cutting	Total Tonnage	Daymen		Total	Total Labor
				Inside	Outside		
Minimum.....	0.36	0.014	0.43	0.17	0.03	0.27	0.84
Maximum.....	2.01	0.86	2.01	1.23	0.66	1.45	3.38
Average, 1921.....							1.91
As between Union and Non-union Mines for Mines Given							
Union:							
Minimum.....	0.55	0.07	0.68	0.24	0.03	0.27	1.14
Maximum.....	2.01	0.86	2.01	0.95	0.45	1.40	3.38
Non-union:							
Minimum.....	0.36	0.014	0.43	0.17	0.07	0.34	0.84
Maximum.....	1.43	0.25	1.42	1.23	0.66	1.45	2.39
As Regards Size of Mine—Less than 1000 Tons Output per Day							
Minimum.....	0.46	0.016	0.50	0.17	0.07	0.41	1.10
Maximum.....	2.01	0.86	2.01	1.23	0.66	1.45	3.06
Average, 1921.....							1.83
Between 1000 and 2000 Tons Output per Day							
Minimum.....	0.36	0.014	0.43	0.26	0.08	0.37	0.84
Maximum.....	1.28	0.14	1.41	0.87	0.34	1.37	2.25
Average, 1921.....							1.72
Over 2000 Tons Output per Day							
Minimum.....	0.43	0.03	0.46	0.24	0.03	0.27	1.13
Maximum.....	1.14	0.16	1.26	0.64	0.24	0.79	1.95
Average, 1921.....							1.72
As Regards Thickness of Seam Worked							
Seams 48 in. and less in thickness:							
Minimum.....	0.39	0.03	0.43	0.17	0.07	0.42	0.84
Maximum.....	1.77	0.25	1.79	0.845	0.665	1.20	2.51
Average, 1921.....							2.41
Seams 49 in. to 72 in. in thickness:							
Minimum.....	0.36	0.018	0.43	0.26	0.07	0.35	0.90
Maximum.....	1.6	0.86	1.77	1.23	0.52	1.45	2.49
Average, 1921.....							1.86
Seams 73 in. to 110 in. in thickness:							
Minimum.....	0.43	0.014	0.48	0.24	0.08	0.33	0.95
Maximum.....	2.01	0.16	2.01	0.98	0.34	1.18	3.06
Average, 1921.....							1.54

NOTE.—Average 1921 figures are calculated from data in report of U. S. Coal Commission.

TABLE 2.—*Production Data, West Virginia Mines*

Mine	County	Union or Non-union	Name of Seam	Thick-ness Inches	Month	Production Net Tons	No. Days Worked	Aver. Prod. per Day
1	Raleigh	Non-union	Beekley	60.0	May, 1922	43,627	22 2	1,965
2	Raleigh	Non-union	Beekley	60.0	June, 1922	43,698	19.2	2,276
3	Raleigh	Non-union	Beekley	54 0	May, 1922	15,182	25 0	605
4	Raleigh	Non-union	Beekley	54 0	June, 1922	15,419	21 5	717
5	Raleigh	Non-union	No. 3	45 0	May, 1922	37,616	25 4	1,481
6	Raleigh	Non-union	No. 3	45 0	June, 1922	33,143	20 8	1,593
7	Raleigh	Non-union	No. 3	54.0	May, 1922	11,955	25 4	471
8	Raleigh	Non-union	No 3	54.0	June, 1922	11,821	20.6	574
						31,735-M 941-P		
9	Logan	Non-union	Island Creek	79.0	Mar., 1922	32,876	26.0	1,267
						42,258-M 7,483-P		
10	Logan	Non-union	Island Creek	81.0	Mar., 1922	49,741	26 0	1,913
						30,783-M 1,987-P		
11	Logan	Non-union	Island Creek	75.0	Mar., 1922	32,770	25.9	1,267
12	Logan	Non-union	Island Creek	77.0	Mar., 1922	40,146- <sup>4</sup>	26 0	1,544
						2,925-P 88,385-M		
13	Raleigh	Non-union	Beekley	60.0	Mar., 1922	41,310	24.8	1,669
14	Mingo	Non-union	Thacker	66.0	Mar., 1922	27,001	24.0	1,125
						Island Creek 46.0		
15	Logan	Non-union	Eagle	60.0	June, 1922	37,255- <sup>4</sup>	26.0	1,433
						Island Creek 43.0		
16	Logan	Non-union	Eagle	72.0	June, 1922	11,026- <sup>4</sup>	26.0	424
						12,170-M 4,732-P		
17	McDowell	Non-union	Sewell	40.0	Mar., 1922	16,902	24.0	704
18	Mercer	Non-union	No. 3 Poca.	52.0	Mar., 1922	17,416- <sup>4</sup>	25.0	696
19	McDowell	Non-union	No. 4 Poca.	73.7	May, 1922	23,655	27.0	876
20	McDowell	Non-union	War Creek	50.0	May, 1922	19,000	27.0	704
21	Mingo	Non-union	Thacker	51.0	May, 1922	21,273- <sup>4</sup>	27.0	788
22	Mingo	Non-union	Thacker	52.0	June, 1922	4,032	26.0	155
23	Mingo	Non-union	Alma	57.0	June, 1922	5,146	24.0	214
24	Mingo	Non-union	Thacker	49.0	June, 1922	11,847	25.0	474
						74,402-C 1,100-S		
25	Marion	Union	Pittsburgh	96.0	Nov., 1921	75,502	25.0	3,020
26	Marion	Union	Pittsburgh	85.0	Mar., 1922	25,585	23.0	1,112
27	McDowell	Non-union	No. 3 and No 4 Poca.		May-June, 22	1,027,795		

<sup>1</sup> 49,253 tons machine coal; large part of this was cut by loaders, by punching machines<sup>2</sup> 65 per cent. robbing, no machines used.<sup>3</sup> 45 per cent. robbing, no machines used.<sup>4</sup> All machine coal.

M, machine mined.

P, pick mined.

C, coal.

S, slate.

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TABLE 2.—Continued

Mine	Men Working per Day						Average Production Net Tons							
	Load-ers	Mach Men	Total Ton-nage Men	Daymen			Total All Men	Load-ers	Mach Men (2)	Total Ton-nage Men	Daymen			Total All Men
				In-side	Out-side	Total					In-side	Out-side	Total	
1	118.0	8.0	126.0	98.0	46.0	144.0	270.0	16.7	491	15.59	20.1	42.7	13.64	7.28
2	121.0	8.0	129.0	103.0	44.0	147.0	276.0	18.8	569	17.64	22.1	51.7	15.48	8.25
3	38.0	4.0	42.0	34.0	17.0	51.0	93.0	15.9	302	14.40	17.8	35.6	11.86	6.50
4	41.0	4.0	45.0	37.0	17.0	54.0	99.0	17.5	350	15.93	19.4	42.2	13.28	7.24
5	81.0	8.0	89.0	60.0	23.0	83.0	172.0	18.3	370	16.64	24.7	64.4	17.84	8.61
6	77.0	8.0	85.0	59.0	23.0	82.0	167.0	20.7	398	18.74	27.0	69.3	19.43	9.53
7	36.0	4.0	40.0	28.0	15.0	43.0	83.0	13.1	235	11.77	16.8	31.4	10.95	5.67
8	43.0	4.0	47.0	34.0	18.0	52.0	90.0	13.3	287	12.20	16.9	31.9	11.04	5.80
9	69.0	8.0	77.0	4.0	23.0	67.0	144.0	18.2	204	16.32	28.6	54.7	18.76	8.73
10	125.0	10.0	135.0	80.0	16.0	96.0	231.0	15.3	324	14.17	23.9	119.6	19.93	8.22
11	60.0	8.0	68.0	47.0	19.0	66.0	134.0	21.1	296	18.63	27.0	66.7	19.20	9.45
12	105.0	10.0	115.0	53.0	18.0	71.0	186.0	14.7	309	13.43	29.1	85.8	21.75	8.30
13	120.0	15.0	135.0	101.0	17.0	118.0	253.0	13.9	207	12.36	16.5	98.2	14.14	6.60
14	68.0	12.0	80.0	122.0	71.0	193.0	273.0	16.5	187	14.06	9.2	15.8	5.83	4.12
15	103.4	11.9	115.3	67.8	30.0	97.8	213.0	13.9	241	12.43	21.1	47.8	14.65	6.73
16	29.8	5.0	34.8	44.6	14.2	58.8	93.6	14.2	170	12.18	9.5	30.0	7.21	4.52
17	70.6	4.0	74.6	15.3	21.5	36.8	111.4	10.0	254- <sup>3</sup>	9.44	46.0	32.8	19.13	6.3
18	49.6	6.0	55.6	31.6	25.7	57.3	112.9	14.0	104- <sup>3</sup>	12.52	22.0	27.1	12.15	6.16
19	114.0	2.0	116.0	83.0	35.0	118.0	234.0	7.68	976	7.52	10.55	25.03	7.42	3.74
20	66.0	8.0	74.0	56.0	31.0	87.0	161.0	10.67	176	9.51	12.57	22.71	8.09	4.37
21	45.1	6.0	51.1	71.6	14.0	85.6	136.7	17.5	263	15.42	11.0	56.3	9.20	5.76
22	10.4	2.0	12.4	13.4	7.0	20.4	32.8	15.0	155	12.5	11.6	22.1	7.60	4.72
23	17.4	4.0	21.4	24.8	14.0	38.8	60.2	12.3	107	10.00	8.6	15.3	5.51	3.55
24	30.1	4.0	34.1	73.3	11.0	84.3	118.4	15.7	237	13.90	6.5	43.1	5.62	4.00
106-P														
181-M														
25	287	44.0	331.0	238.0	66.0	304.0	635.0	10.5	90- <sup>1</sup>	9.12	12.7	45.8	9.93	4.75
26	87.0	16.0	103.0	58.0	15.0	73.0	176.0	12.78	139	10.80	19.17	74.13	15.23	6.32
27								19.0	200					

Coal Loading.—In June, 1922, at Mine No. 15 in Logan County, one (1) man loaded 683 mine cars holding 956.2 net tons coal in 298 hr. spent in the mine. Loader worked in double track rooms 36 ft. wide, coal averaged 46 in. thick; he drilled and shot his coal about  $\frac{3}{4}$  of the time, but neither picked out impurities nor set props. Besides this he did 10 hr. of day labor; his total earnings for the month were \$519.93. Average loading per hour = 3.2 tons or 2.3 mine cars.



TABLE 2.—Continued

Mine	Man-hours per Net Ton				Greatest Tonnage Loaded in One Day	Can Loaders Produce More with Full Car Supply?	Loaders' Duties	
	Loaders	Mach. Men	Total Tonnage Men	Daymen				
				Inside				Outside
1	0.48	0.03	0.51	0.40	0.19	0.59	1.10	Drill, shoot, timber, clean coal, no trackwork (8 hr.).
2	0.43	0.03	0.46	0.36	0.15	0.51	0.97	Drill, shoot, timber, clean coal, no trackwork (8 hr.).
3	0.50	0.05	0.55	0.45	0.22	0.67	1.23	Drill, shoot, timber, clean coal, no trackwork (8 hr.).
4	0.46	0.04	0.50	0.41	0.19	0.60	1.10	Drill, shoot, timber, clean coal, no trackwork (8 hr.).
5	0.44	0.04	0.48	0.32	0.12	0.44	0.93	Drill, shoot, timber, clean coal, no trackwork (8 hr.).
6	0.39	0.04	0.43	0.30	0.12	0.43	0.84	Drill, shoot, timber, clean coal, no trackwork (8 hr.).
7	0.61	0.07	0.68	0.48	0.25	0.73	1.41	Drill, shoot, timber, clean coal, no trackwork (8 hr.).
8	0.60	0.06	0.65	0.47	0.26	0.72	1.37	Drill, shoot, timber, clean coal, no trackwork (8 hr.).
9	0.50	0.05	0.55	0.32	0.16	0.48	1.03	Shoot, do not drill coal, no trackwork or timbering, clean coal (9 hr.).
10	0.59	0.04	0.63	0.38	0.08	0.45	1.08	Shoot, do not drill coal, no trackwork or timbering, clean coal (9 hr.).
11	0.43	0.05	0.48	0.33	0.15	0.47	0.95	Shoot, do not drill coal, no trackwork or timbering, clean coal (9 hr.).
12	0.61	0.06	0.67	0.31	0.11	0.41	1.08	Shoot, do not drill coal, no trackwork or timbering, clean coal (9 hr.).
13	0.65	0.08	0.73	0.55	0.09	0.64	1.36	Drill, and shoot, timber, but do not lay track.
14	0.49	0.09	0.57	0.37	0.51	1.37	37.8	Drill, shoot, and timber.
15	0.65	0.07	0.72	0.48	0.16	0.61	1.34	Drill, shoot, and timber, no trackwork (9 hr.).
16	0.63	0.11	0.74	0.95	0.30	1.25	1.99	Drill, shoot, and timber, no trackwork (9 hr.).
17	0.80	0.06	0.85	0.17	0.24	0.43	1.27	Drill, shoot, timber, lay room track.
18	0.57	0.07	0.64	0.36	0.29	0.65	1.29	Drill, shoot, timber, lay room track.
19	1.04	0.02	1.06	0.758	0.32	1.08	2.14	Drill, timber, lay track and clean dirt; do not shoot.
20	0.75	0.09	0.84	0.64	0.35	0.99	1.83	Drill, timber, lay track and clean dirt; and shoot coal.
21	0.46	0.06	0.52	0.73	0.14	0.87	1.38	Load, coal only.
22	0.53	0.10	0.63	0.70	0.36	1.06	1.99	Load, coal only.
23	0.65	0.15	0.80	0.93	0.52	1.45	2.25	Load, coal only.
24	0.51	0.07	0.58	1.23	0.19	1.42	2.00	Load, coal only.
25	0.76	0.12	0.88	0.63	0.16	0.79	1.67	Timber, and lay straight track; do not drill or shoot.
26	0.63	0.12	0.75	0.42	0.11	0.53	1.27	Timber, drill, shoot coal, lay track, and clean dirt.
27	0.44	0.08	0.52	0.54	0.23	0.83	1.36	

In June, 1922, at Mine No. 16 in Logan Co., one (1) man loaded 572 mine cars holding 743.6 net tons coal in 222 hr. spent in the mine. Loader worked in two entries 18 ft. wide, coal averaged 44 in. thick; he drilled and shot his coal, but neither picked out impurities nor set timbers. Roof conditions in these working places were not favorable with considerable water present. Besides this, he did 2 days or 18 hr.-day work; his total earnings for the month, including pay for water at face, were \$528.50. Average loading per hour = 3.4 tons or 2.5 mine cars.

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TABLE 3.—*Production Data, Kentucky Mines*

Mine	County	Union or Non-union	Name of Seam	Thick-ness, Inches	Month	Production Net Tons	No. Days Worked	Aver. Prod. per Day
1	Eastern Kentucky	Non-union	Miller Cr. No. 1	47	Aug., '21	6,232-C 352-S 6,584 14,835-C 2,442-S	24.25	272
2	Eastern Kentucky	Non-union	Miller Cr. No. 1	48	Aug., '21	17,277 17,643-C 6,611-S	23.75	727
3	Eastern Kentucky	Non-union	Elkhorn	89	May, '22	24,254 16,138-C 4,906-S	27.0	898
4	Eastern Kentucky	Non-union	Elkhorn	96	June, '21	21,044 12,800-C 4,804-S	26.0	809
5	Eastern Kentucky	Non-union	Elkhorn	89	June, '21	17,604 34,580-C 3,373-S	26.0	677
6	Eastern Kentucky	Non-union	Elkhorn	96	Mar., '22	38,458 21,877-C 3,698-S	27.0	1,424
7	Eastern Kentucky	Non-union	Elkhorn	110	June, '21	25,075 23,437-C 3,540-S	26.0	964
8	Eastern Kentucky	Non-union	Elkhorn	101	May, '22	27,027 24,859-C 3,182-S	27.0	1,001
9	Eastern Kentucky	Non-union	Elkhorn	91	Mar., '22	28,041 20,153-C 3,184-S	27.0	1,039
10	Eastern Kentucky	Non-union	Elkhorn	74	June, '21	23,337 5,028-C 1,070-S	26.0	898
11	Eastern Kentucky	Non-union	Elkhorn	100	June, '22	6,098 26,418-C 4,722-S	25.0	244
12	Eastern Kentucky	Non-union	Elkhorn	80	Mar., '22	31,140 13,829-C 1,346-S	27.0	1,153
13	Eastern Kentucky	Non-union	Elkhorn	83	June, '21	15,175 34,440-C* 2,376-S	26.0	584
14	Eastern Kentucky	Non-union	Pond Cr.	60		36,816	20.0	1,841
15	Eastern Kentucky	Non-union	No. 6	70	May, '22	57,020*	21.4	2,664
16	Eastern Kentucky	Non-union	No. 6	70	Aug., '21	58,553*	25.5	2,296
17	Western Kentucky	Union	No. 9	58	May, '22	22,168*	24.8	894
18	Western Kentucky	Union	No. 11	72	May, '22	20,757*	27.0	769
19	Western Kentucky	Union	No. 11	72	May, '22	38,651*	24.1	1,604
20	Western Kentucky	Union	No. 9	57	May, '22	63,700*	26.0	2,450
21	Western Kentucky	Union	No. 9	53	May, '22	40,810*	24.5	1,666

\* All machine coal.

Coal Loading.—At mines Nos 15 and 16 in Perry County; Loader A in 25 days loaded 709 net tons coal; average, 28.5 tons per day; Loader B in 21 days loaded 539 net tons coal; average, 25.5 tons per day.

TABLE 3.—Continued

Mine	Men Working per Day					Average Production Net Tons per Day					Man-hours per Net Ton										
	Load-ers	Mach. Men	Daymen			Total All Men	Load-ers	Mach. Men (2)	Total Ton-nage Men	Daymen		Total All Men	Load-ers	Mach. Men	Daymen		Total Ton-nage Men	Total All Men			
			In-side	Out-side	Total					In-side	Out-side				Total						
1	27.0	4	31.0	20.0	11.0	31.0	62.0	10.07	136	8.77	13.6	24.73	8.77	4.39	0.704	0.12	0.91	0.59	0.32	0.91	1.82
2	69.0	10	79.0	47.0	26.0	73.0	152.0	10.54	145	9.20	15.47	27.96	9.92	4.78	0.76	0.11	0.87	0.52	0.29	0.81	1.93
3	73.0	2	75.0	57.0	22.0	79.0	154.0	12.30	898	11.97	15.75	40.77	11.37	5.83	0.65	0.018	0.07	0.51	0.19	0.70	1.87
4	83.0	1	84.0	53.0	15.0	68.0	152.0	9.75	809	9.32	15.26	53.03	11.90	6.32	0.82	0.09	0.91	0.52	0.15	0.67	1.53
5	86.0	2	88.0	50.0	15.0	65.0	153.0	7.87	676	7.69	13.54	45.13	10.41	4.42	1.02	0.02	1.04	0.59	0.18	0.77	1.81
6	170.0	3	173.0	92.0	27.0	119.0	292.0	8.38	949	8.23	15.43	52.74	11.97	4.88	0.955	0.017	0.97	0.52	0.15	0.97	1.64
7	107.0	3	109.0	64.0	25.0	89.0	198.0	9.01	964	8.84	15.06	38.56	10.83	4.87	0.887	0.016	0.905	0.533	0.21	0.74	1.64
8	98.0	2	95.0	63.0	21.0	84.0	179.0	10.76	1001	10.54	15.89	47.07	11.92	5.59	0.74	0.016	0.756	0.50	0.17	0.67	1.43
9	108.0	3	111.0	76.0	20.0	96.0	207.0	9.62	692	9.36	13.67	51.05	10.82	5.01	0.83	0.023	0.85	0.58	0.15	0.74	1.60
10	117.0	2	119.0	67.0	24.0	91.0	210.0	7.97	898	7.55	13.40	37.42	9.87	4.28	1.04	0.018	1.06	0.58	0.214	0.81	1.86
11	85.0	2	87.0	30.0	6.0	36.0	73.0	6.97	244	6.59	8.13	40.00	6.78	3.34	1.15	0.035	1.21	0.98	0.196	1.18	2.29
12	125.0	2	127.0	69.0	26.0	95.0	222.0	9.22	1153	9.03	16.71	44.35	12.14	5.10	0.87	0.014	0.88	0.478	0.18	0.66	1.54
13	61.0	2	63.0	45.0	10.0	55.0	118.0	9.57	684	9.27	12.98	58.4	10.62	4.95	0.835	0.027	0.86	0.616	0.137	0.75	1.61
14	81.7	16	97.7	72.4	36.2	108.6	206.3	22.5	230	18.84	25.4	50.8	10.95	8.9	0.36	0.07	0.43	0.31	0.16	0.47	0.90
15	153.0	28	186.0	123.0	66.0	189.0	375.0	16.9	190	14.32	21.7	40.4	14.10	7.1	0.47	0.08	0.55	0.37	0.20	0.57	1.13
16	155.0	28	183.0	114.0	69.0	183.0	366.0	14.8	164	12.55	20.0	33.3	12.55	6.3	0.54	0.10	0.64	0.40	0.24	0.64	1.28
17	92.0	12	104.0	53.0	13.0	66.0	170.0	9.7	149	8.60	16.9	68.8	13.54	5.3	0.83	0.11	0.94	0.47	0.12	0.59	1.53
18	60.0	8	68.0	39.0	12.0	41.0	109.0	12.8	192	11.81	26.5	64.1	18.76	7.1	0.63	0.09	0.72	0.30	0.12	0.42	1.14
19	150.0	18	168.0	77.0	33.0	110.0	278.0	10.7	178	9.55	20.8	48.6	14.58	5.8	0.75	0.09	0.84	0.38	0.16	0.54	1.38
20	238.0	28	266.0	97.0	35.0	132.0	398.0	10.3	175	9.21	25.3	70.0	18.56	6.2	0.78	0.09	0.867	0.32	0.114	0.431	1.29
21	166.0	20	186.0	57.0	21.0	78.0	264.0	10.0	167	8.96	29.2	79.3	21.35	6.3	0.80	0.10	0.893	0.26	0.10	0.374	1.27

Loader C in 26 days loaded 706 net tons coal; average, 26.3 tons per day; Loader D in 23 days loaded 710 net tons coal; average, 27.3 tons per day; Loader E in 22 days loaded 913 net tons coal; average, 41.5 tons per day. Total, 119 days loaded 3877 net tons coal; average, 30.1 tons per day.

Loader C in 25 days loaded 706 net tons coal; average, 28.3 tons per day; Loader D in 26 days loaded 710 net tons coal; average, 27.3 tons per day; Loader E in 22 days loaded 913 net tons coal; average, 41.5 tons per day. Total, 119 days loaded 8677 net tons coal; average, 30.1 tons per day.

TABLE 3.—*Continued*

Mine	Greatest Tonnage Loaded in One Day	Can Loaders Produce More with Full Car Supply?	Remarks
1	29 0		Loaders, with exception of machine, load, drill, shoot.
2	30.0		All loaders timber, lay track and clean dirt.
3	39 8		Same as No. 1.
4	29 9	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
5	24.45	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
6	30 5	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
7	32.3	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
8	36.4	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
9	28.85	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
10	35 35	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
11	25 55	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
12	26 2	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
13	31 6	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
14	42.0	Yes	Loaders drill, timber, lay track and clean dirt; do not shoot.
15	39 0		Loaders load only, but clean 8-in. laminated coal.
16	41 0		Loaders timber and lay straight room track.
17	24.3		Loaders timber and lay straight room track.
18	24.8	Yes	Loaders drill, clean coal, set timbers and pay for one-half shooting.
19	22.4	Not this month	Loaders drill, clean coal, set timbers and pay for one-half shooting.
20		Yes	Loaders drill, clean coal, set timbers and pay for one-half shooting.
21			Loaders drill, shoot coal, timber, but do no track work.

Working time was 8 hr. per day. In addition to loading coal, the loader only lays "jumpers" in the face of his room. Drilling, shooting, timbering and straight track work is done by the company. Loader E earnings, in month given (January, 1921) were \$547 80.

of labor of 0.644 man-hour, or slightly less than 77 per cent. of the best total figure shown by these data.

A study of the data presented shows that with the proper organization and with carefully planned mining methods, the average amount of coal loaded per day, *where this amount is not restricted by outside regulations*, can be increased at least 25 per cent. without a corresponding increase in the amount of day labor needed.

TABLE 4.—*Production Data, Maryland Mines (Union)*

Mine	County	Name of Seam	Thickness, Inches	Production, Net Tons	No. Days Worked	Aver. Prod. per Day	Men Working per Day					Average Production Net Tons per Day								
							Load-ers	Mach. Men	Total Tonnage Men	Daymen		Total All Men	Load-ers	Mach. Men (2)	Total Tonnage Men	Daymen		Total All Men		
										In-side	Out-side					In-side	Out-side			
1	Allegany	Sewickley	36	15,107-C 142-S 15,249 15,354-C 1,162-S	24	635	140	2	142	30	20	40	182	4.53	635	4.47	31.75	31.75	15.87	3.49
2	Allegany	Pittsburgh	96	16,516	27	612	154	0	154	03	17	80	234	3.97		3.97	9.71	36.00	7.02	2.61

Mine	Man-hours per Net Ton					Remarks			
	Loaders	Mach. Men	Total Tonnage Men	Daymen			Greatest Tonnage Loaded in One Day		
				Inside	Outside			Total	
1	1.77	0.03	1.79	0.25	0.25	0.50	2.29	12.11-P	Loaders, with exception of machine, load, drill and shoot coal.
2	2.01	....	2.01	0.82	0.22	1.05	3.06	14.5-M 13.9	All loaders timber, lay track and clean dirt. Loaders drill, shoot coal, timber, lay track and clean dirt.



816 DATA ABOUT LABOR EMPLOYED IN VARIOUS BITUMINOUS COAL MINES

TABLE 6.—*Production Data, Pennsylvania Mines*

Mine	County	Union or Non-union	Name of Seam	Thick-ness, Inches	Month	Produc-tion Net Tons	No. Days Worked	Aver. Prod. per Day
1	Somerset	Non-union	Pittsburgh	70	Mar., '22	22,027	23	958
2	Somerset	Non-union	C'	48	Mar., '22	16,184	24	674
3	Somerset	Non-union	C'	51	Mar., '22	31,147	23	1354
4	Somerset	Non-union	C'	45	Mar., '22	26,645	25	1066
5	Somerset	Non-union	E	41	Mar., '22	16,097	25	644
						9,370-P 14,534-M		
6	Westmoreland	Non-union	Pittsburgh	85	Jan., '23	23,904 28,135-P 9,378-M	26	919
7	Westmoreland	Non-union	Pittsburgh	86	Mar., '23	37,513	24	1563
8	Greene	Non-union	Pittsburgh	76	Dec., '22	33,771*	25	1551
9	Fayette	Non-union	Pittsburgh	84				
10	Somerset	Open-shop	B	42	Mar., '23	41,777	27	1547
11	Somerset	Open-shop	B	44	Mar., '23	42,210	27	1556

Mine	Men Working per Day						Average Production Net Tons per Day							
	Load-ers	Mach. Men	Total Ton-nage Men	Daymen			Total All Men	Load-ers	Mach. Men (2)	Total Ton-nage Men	Daymen			Total All Men
				In-side	Out-side	Total					In-side	Out-side	Total	
		All Pick												
1	171		171	51	23	74	245	5.602		5.602	18.78	41.65	12.94	3.91
2	102	3	105	45	56	101	206	6.61	449	6.42	14.98	12.03	6.67	3.27
3	181	3	184	79	7	79	263	7.48	903	7.36	17.14		17.14	3.15
4	171	17	188	81	30	111	299	6.23	135	5.67	13.16	35.53	9.60	3.56
5	95	20	115	68	21	89	204	6.80	64	5.70	9.47	30.67	7.24	3.16
6	72	8	80	36	30	66	146	12.8	140	11.5	25.5	30.6	13.9	6.3
7	142	5	147	99	67	166	313	11.0	156	10.63	15.8	23.3	9.41	5.0
8	177	13	195	142	66	208	403	8.8	172	7.95	10.9	23.5	7.46	3.8
9								20.0						
10	242-P		242	139	36	175	417	6.4		6.4	11.1	43.0	8.84	3.7
11	232	23	255	119	33	152	407	6.7	135	6.10	13.1	47.1	10.30	3.8

\* All machine coal.

TABLE 6.—*Continued*

Mine	Man-hours per Net Ton							Greatest Tonnage Loaded in One Day
	Loaders	Maoh. Men	Total Tonnage Men	Daymen			Total All Men	
				Inside	Outside	Total		
1	1.428		1.428	0.425	0.192	0.617	2.045	17
2	1.21	0.036	1.25	0.534	0.665	1.20	2.45	16 1-P 25.25-M
3	1.07	0.018	1.09	0.466		0.466	1.55	17.15-P 18.55-M
4	1.28	0.127	1.41	0.607	0.225	0.833	2.247	21.0-P 15.85-M
5	1.18	0.25	1.40	0.845	0.261	1.11	2.51	14.45-P 19.8-M
6	0.61	0.11	0.695	0.31	0.26	0.575	1.27	40-M
7	0.73	0.10	0.752	0.51	0.34	0.850	1.60	32-P
8	0.91	0.09	1.01	0.73	0.34	1.07	2.10	34
9	0.45							
10	1.25		1.25	0.72	0.18	0.905	2.16	22
11	1.19	0.12	1.31	0.61	0.17	0.777	2.11	21

Mine	Can Loaders Produce More with Full Car Supply?	Remarks
1	Yes	Loaders drill, shoot coal, timber, lay track and clean dirt.
2	Yes	Loaders drill, shoot coal, timber, lay track and clean dirt.
3	Yes	Loaders drill, shoot coal, timber, lay track and clean dirt.
4	Yes	Loaders drill, shoot coal, timber, lay track and clean dirt.
5	Yes	Loaders drill, shoot coal, timber, lay track and clean dirt.
6		Loaders drill, shoot coal, timber, lay straight track.
7		Loaders drill, shoot coal, timber, lay straight track.
8		Loaders drill, timber and lay track.
9		Loaders lay track and set timbers.
10		Loaders drill, shoot coal, timber and lay room track
11		Loaders drill, shoot coal, timber and lay room track.

At Mine No. 9, in Fayette County, pick miner loading average for past years is 11 net tons daily; loader average after air puncher mining machine is approximately 17 net tons per day; loader average after electric shortwall mining machine is approximately 20 net tons per day. Pick miners lay track, set timbers and drill holes; machine loaders lay track, set timbers but drill no holes—neither class handles much slate. Roof coal or draw slate are left up in working places. Empty cars are delivered to the face of working places.



TABLE 7.—*Production Data, Virginia Mines, for May, 1922 (Non-union)*

Mine	County	Name of Seam	Thickness, Inches	Production Net Tons Worked	No Days Worked	Aver. Prod. per Day	Men Working per Day					Average Production Net Tons per Day								
							Load-ers	Mach Men	Total Tonnage Men	Daymen		Total All Men	Load-ers	Mach. Men (3)	Total Tonnage Men	Daymen		Total All Men		
										In-side	Out-side					In-side	Out-side			
1	Dickinson	Upper-Banner	66	65,572*	26	2522	242	20	202	203	43	216	508	10.4	252	9.625	12 1/2	58.7	10.25	5.0
2	Dickinson	Upper-Banner	45	14,674*	27	543	70	10	80	29	5	31	11 1/2	7.7	109	6.78	18.7	109.0	15.91	4.8
Mine	Man-hours per Net Ton										Greatest Tonnage Loaded in One Day	Remarks								
	Loaders	Mach. Men	Total Tonnage Men	Daymen		Total All Men														
				Inside	Outside															
1	0.77	0.06	0.831	0.64	0.14	0.780	1.6	24	Loaders shoot, do not drill. Set safety posts only and lay straight track.											
2	1 04	0.15	1.179	0.43	0.07	0.503	1.67	16												

\* All machine coal.

TABLE 8.—*Production Data, Indiana Mines (Union)*

Mine	Men Working per Day					Average Production Net Tons per Day															
	County	Name of Seam	Thickness, Inches	Month	Production, Net Tons	No. Days Worked	Aver. Prod. per Day	Daymen			Total All Men	Load-ers	Mach. Men (2)	Total Ton-nage Men	Daymen		Total All Men				
								Load-ers	Mach. Men	Total Ton-nage Men					In-side	Out-side		Total			
1	Knox	5	78	Dec., '22	89,262*	16.0	5579	516.0	48.0	564.0	165	72.0	237	801.0	10 8*	232	9.89	33 8	72 5	23.54	6.9
2	Knox	5	78	Mar., '23	59,165*	14.0	4226	326.0	44.0	370.0	127	48.0	175	545.0	13 0*	192	11.42	33.3	88 0	24.14	7.75
3	Sullivan	6	60	Mar., '22	13,596	18.62	730	75.3	11.5	86.8	86.5	41.0		214.3	9 7	127	8.41	8 4	17 8		3.4

Mine	Man-hours per Net Ton					Greatest Tonnage Loaded in One Day	Can Loaders Produce More with Full Car Supply?	Loaders' Duties		
	Loaders	Mach. Men	Total Tonnage Men	Daymen					Total All Men	
				Inside	Outside	Total				
1	0.74	0.07	0.809 *	0.24	0.11	0.339	1.16	16	Yes	Drill, prepare shots, clean coal, timber, no track-work.
2	0.615	0.083	0.698	0.24	0.00	0.331	1.03	22	Yes	Drill, prepare shots, clean coal, timber, no track-work.
3	0.82	0.013	0.095	0.095	0.045	1.40	2.35			Drill, shoot, timber, no trackwork.

\* Local union has limit of four cars per man per day.



TABLE 9.—(Continued)

Mine	Man-hours per Net Ton						Greatest Tonnage Loaded in One Day	Can Loaders Produce More with Full Car Supply?	Loaders' Duties
	Loaders	Mach. Men	All Ton- nage Men	Daymen		Total All Men			
				Inside	Outside				
1	0.86	0.13	0.96	0.50	0.19	0.69	1.63		Drill, shoot, timber, no trackwork.
2	0.67	0.08	0.75	0.37	0.11	0.48	1.23		Drill, shoot, timber, no trackwork.
3	0.73	0.16	0.89	0.37	0.11	0.48	1.31		Drill, shoot, timber, no trackwork.
4	0.55	0.13	0.68	0.39	0.12	0.51	1.18		Drill, shoot, timber, no trackwork.
5	0.82	0.08	0.90	0.65	0.26	0.91	1.82		Drill, shoot, timber, no trackwork.
6	0.82	0.08	0.90	0.51	0.19	0.70	1.60		Drill, shoot, timber, no trackwork.
7	1.14	0.12	1.26	0.54	0.17	0.71	1.95		Drill, shoot, timber, no trackwork.
8	0.81	0.14	0.95	0.47	0.18	0.65	1.60		Drill, shoot, timber, no trackwork.
10*							18.2	10 best = 15 tons	

\* From Coal Age, April 13, 1923.

TABLE 9.—(Continued)

District	Number of Mines	Period	Production Net Tons	No. Days Worked	Aver. Prod. per Day	Men Working per Day				Average Production Not Tons per Day				Man-hours per Net Ton					Greatest Tonnage Loaded in One Day	
						Loaders	Mach Men	All Tonnage Men	Total Day- men	Total All Men	Loaders	Mach. Men (2)	All Top- nage Men	Total Day- men	Total All Men	Loaders	Mach. Men	All Top- nage Men		Daymen
1	7	Year—1920	1,456,068	260	5,600			2,410	1,214	3,024			4.08	5.73				1.06	1.30	3.38
2	11	Year—1920	1,915,462	259	7,306			1,990	1,392	3,382			6.97	10.01				1.14	0.70	1.94
3	13	Year—1920	3,900,031	254	15,353			4,460	2,710	7,170			6.94	11.90				1.15	0.67	1.82
4	26	Year—1920	13,340,068	232	57,500			10,177	8,191	18,368			9.43	12.21				0.85	0.65	1.51
5	6	Year—1920	2,163,696	281	7,344			157	114	3,423				17	90			?	?	1.81
6	27	Year—1920	6,658,320	201	33,228			5,660	3,877	9,537	†							0.90	0.71	1.01
7†	46	Year—1920	18,493,064	219	84,443	10,474	1570	18,044	15,049	33,698	10.2	107.0	9.32	9.4	4.7	0.78	0.07	0.86	0.85	1.71
State†	135	Year—1920	47,927,209	230	208,399	36,589	3,487	40,076	30,842	70,918	5.71	120.0	5.21	6.77	2.95	1.40	0.13	1.54	1.18	2.71
7†	52	Year—1921	18,523,933	159	116,503	21,869	2084	23,953	18,300	42,253	10.2	107.0	8	6	4.95	0.78	0.08	0.93	1.71	
State†	140	Year—1921	38,205,778	146	263,433	48,225	4596	52,821	33,404	86,225	9.3	97.8	9.3	11.0	18.2			0.86	0.81	1.78
State		Jan.—Mar., incl '22	10,364,378																	

† Second set of figures for each year includes mines in Districts 1, 2, 3, 4, 5, 6, 7.

‡ Data incomplete.

**NOTE.**—The unit figures for 1920 are all slightly higher than the actual figure, as the tonnages include some mines not reporting the days worked. All base data from Coal Operators Assos. Bulletins.

*District 1*—The No. 2 seam is worked almost entirely by longwall, pick miners in small shaft operations that could not compete with the rest of the state if they were not so close to Chicago. The seam is from 2 ft. 6 in. to 4 ft 0 in thick, averaging about 3 ft. 4 in and has irregular streaks of dirt and sulfur in it, as thick as 4 in. Roof conditions are poor. Grades are slight in most of the district.

*District 2*—No. 1 seam averages 4 ft. thick and is much broken by small faults, slips and clay veins. It has numerous sulfur bands in local places. The roof is usually good, the fireclay bottom heaves badly when wet.

No. 2 seam is the same as in District 1.

No. 5 seam is from 4 to 8 ft thick, averaging 4 ft 8 in, with discontinuous bands of pyrites over the middle of the seam. The gray fireclay bottom heaves badly when air slaked. In local sections, a thin layer of iron pyrites on top of the coal keeps the roof up.

*District 3*—No. 5 seam is the same as in District 2.

No. 6 seam averages about 6 ft. thick and has a band of iron pyrites about 2 in. thick, in the lower part of the seam. It has a hard clay bottom and a shale top disintegrates with exposure.

*District 4*—No. 6 seam is about the same as in District 3 and furnishes nearly all the production in this district.

*District 5*—No. 6 seam is about the same as in Districts 3 and 4, except that the roof is always shale and falls easily; the bottom is soft fireclay.

No. 7 seam is from 2 ft. 6 in. to 7 ft. 6 in. thick and averages about 5 ft. 6 in. It contains numerous bands and lenses of sulfur. The roof, not generally good, is a black shale; the bottom is soft fireclay.

The two seams share in the district's production.

*District 6*—No. 6 seam supplies almost all the production in this district and averages about 7 ft. thick. It has a quantity of impurities. Its roof and bottom are as in District 5.

*District 7*—Normally District 7 supplies about 40 per cent. of the state output.

No. 5 seam averages about 4 ft. 6 in. thick with, usually, a good roof and bottom. The quality of this coal is best in this district.

No. 6 seam reaches a maximum thickness of 14 ft., varying from 8 to 12 ft. over large areas. It always has the parting of iron pyrites, in the thickest coal the parting is sometimes 4 in. thick, and while the top is not good, usually a foot or more of coal is left up for support.

This district has a number of very large mines, some of them the largest producers in the world.

## DISCUSSION

**HOWARD N. EAVENSON.**—When discussing Mr. Southward's paper, Mr. Raiguel said he understood the labor figures given in my paper applied to clean coal. That is not the case; both the first and the second mines, that is as far as the low amount of labor per ton was required, had coal far from clean. The first mine, it is said in the paper, had an average thickness of about 45 in.; as a matter of fact, the thickness is 2 or 3 in. less than that, although this figure was given by the management of the mine. In that thickness, there is about 3 in. of bone coal, which is frozen to both sides of the clean coal, making it very difficult to clean.

The second lowest mine is thicker but it has from 6 to 8 in. of a hard laminated body that must be picked out and thrown away; it is also difficult to clean. That thickness is given as 60 in. Of all the mines listed, in probably not over 10 or 15 per cent. is the coal clean.

After these figures were prepared, the Coal Commission published its figures of labor required (the average obtained from all of the mines in the country), and from those figures I computed the number of man-hours per ton. We used the basis of 8 hr. per day for the loaders, though we all know that, as a general proposition, they do not work that long;

probably 7 hr. would have been better. When an 8-hr. day was in force, we used that straight through; where a 9-hr. day was in force, we used the 9-hr. figures. So I think the figures are all strictly comparable.

The figures show that the management, as everybody knows, around a coal mine has more to do with the amount of labor employed than the thickness of the seam, because one of the thinnest mines has the lowest labor cost or lowest labor required of any mine we investigated.

GEORGE H. ASHLEY\* Harrisburg, Pa.—So far as these figures go, the thinner beds do not affect labor costs at all; I wish this could have been extended to some mines working the much thinner beds, 36 or 30 inches.

HOWARD N. EAVENSON.—These figures apply only to bituminous mines. Very few of these operate in coal as low as 36 in. unless they have a special market that they can control by reason of low freight rates as against the higher labor costs. As a general proposition, those mines are rather small and were purposely omitted, for generally companies of that kind do not have these data in usable form.

GEORGE H. ASHLEY.—As a member of the Pennsylvania Power Survey Board, I find that the engineers have been picking regions in which the beds are thin, not appreciating the effect that thin beds have on the cost of mining coal. They are afraid to go south of Pittsburgh because of the very high land values, forgetting that the cost of mining the thin beds north of Pittsburgh will several times make up that added cost.

E. A. HOLBROOK,† State College, Pa.—Near Saginaw, Mich., I went into a mine that, at the bottom, had started with about 4 ft. of coal. Worming my way through the workings, like a snake, I reached a section where they were mining coal about 12 in. thick. That, I think, is the thinnest coal mined in this country.

S. A. TAYLOR, Pittsburgh, Pa.—One fact that should be brought out is that most of these thin seams are worked locally; they are not worked in competition with great big seams and over a large area.

In New Brunswick, the custom is to drive the shaft (it is only 35 ft.) every 800 ft. and work out an area 400 ft. square to each shaft; the men pushed the cars. The cost was something over \$7 a ton. To work such veins as that in this country would be out of the question.

One factor suggested by Doctor Ashley cannot be gotten away from even with very careful management; in the Central Pennsylvania district, where they are mining the thin coal, the union scale requires so much for brushing down or digging up the bottom. That factor cannot be changed much because it is a scale regulation and you are limited by the amount

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\* State Geologist.

† Dean, School of Mines.

that you have to take down. Pennsylvania mining laws require that we shall have at least 5 ft. above the rail for the main headings; that means 3 ft. of top must be brushed down.

GEORGE H. ASHLEY.—We made a study of the costs in relation to thickness of bed and found, as I recall now, that mining a 2-ft. bed would cost just about twice as much as mining a 4-ft. bed. A good deal of that cost you cannot get away from.

R. V. NORRIS, Wilkes Barre, Pa.—The most remarkable coal mining proposition that came to the attention of the United States Fuel Administration was a small section in Kansas where they were mining from 10 to 12 in. of coal, in very wet seams, from shafts averaging 100 ft. in depth. The mines were a community affair, they shipped no coal away and brought very little in. The farmers worked the mines during bad weather with the result that less than 12 in. of coal was commercially mineable, as far as that community was concerned.

HOWARD N. EAVENSON (author's reply to discussion).—While these figures were prepared for the specific purpose mentioned, it is evident from the discussion at this meeting, and from remarks made privately to the author, that their publication has aroused considerable interest among mining men in the labor performances at the various mines under their control, which was the purpose of the publication of the paper.

While it is true that the thickness of the seam worked has a great and direct influence on the amount of labor required, it is also true that the variation in amount of labor among mines working seams of the same thickness, due to differences in methods of working and management, is now much more than it should be, and is probably at least as much as that due to differences in thickness. This difference affords ample opportunity for the exercise of the ability of both the operator and the mining engineer.



## Development of Mine Transportation in Clifton-Morenci District

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AND JOHN KIDDIE,† MORENCI, ARIZ.

(New York Meeting, February, 1924)

THE problem of transportation in the Clifton-Morenci district of Arizona has been one of peculiar difficulty and consequently has been an important factor in the cost of mining and treating the ores produced. From the crude beginning made over 50 years ago, many changes have been necessary to keep pace with the increased output of copper.

A heavy-duty haulage system has developed on the original 20-in. track gage to meet the existent metal-mine conditions.

### TOPOGRAPHY

The transportation difficulties of this district may be readily appreciated from the relief map shown in Fig. 1. The northern half of the district is high mountainous country and there is a general but irregular drop toward the southern part, where the country, although still rugged, is in reality a great sloping plain. This is cut by numerous ravines from which the waters, in the rainy season, discharge into the channel of the San Francisco River. A chasm, 1000 ft. deep, has been eroded through the center of the district by Chase Creek, which is flanked by high irregular mountain masses, notably Copper Mountain, American Mountain, Coronado Mountain, and Markeen Mountain. The latter rises 2300 ft. above the bed of the creek.

The San Francisco River has also cut a deep channel, though it is somewhat broader than Chase Creek. Eagle Creek traverses the extreme southwest portion of the area, where it has carved picturesquely through vast volcanic flows.

Faulting has left its mark upon the topography of the district by adding to the irregularities caused by erosion. Strong faults occur at the Coro-

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\* Formerly General Manager, Arizona Copper Co., Ltd.

† Mine Superintendent, Phelps Dodge Morenci Branch.

nado mine and near the Longfellow incline at Morenci. The canyon up which the Morenci Southern Ry. reaches Morenci follows a particularly persistent fault. This fault is closely associated with the principal occurrences of the Morenci ores.



FIG. 1.—RELIEF MAP OF CLIFTON-MORENCI DISTRICT.

The ruggedness of the district made the problem of early railroad construction particularly difficult.

#### GEOLOGY

The geology of the Morenci-Clifton district has been described at length by the U. S. Geological Survey.<sup>1</sup> Attention will be called here chiefly to the position of the orebodies. The oxidized ores of copper

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<sup>1</sup> W. Lindgren: Copper Deposits of the Clifton-Morenci District, Arizona. *Prof. Paper* 43 (1905).

which were mined in the earliest years of the district, have been practically worked out. They occurred mainly in the sediments, for the most part in the Carboniferous limestone, Devonian shale and Ordovician limestone of the higher Paleozoic formation. As these deposits were exhausted, prospecting was extended into the large porphyry stock, with the result that, after considerable discouragement, the efforts of the companies were rewarded by the discovery of high-grade chalcocite ore in sufficient quantities to guarantee the future of the district. As time progressed, disseminated ores of lower grade have been found in the porphyry at increasingly greater distances from the contact with the sedimentary area. These lower grade deposits, which are the result of secondary enrichment, are essentially shallow, occurring in the upper horizons of the porphyry. At Coronado, the ore occurrence is not typical of the Morenci district. Here a true fissure vein occurs along an exceedingly strong East and West fault, and carries chalcocite and cupriferous pyrite in vein matter of crushed quartzite, granite and diabase. Low-grade ore has been found in the main Coronado orebody on the adit level, 1100 ft. below the collar of the Matilda shaft.

Because the ore of the district is comparatively shallow, the main underground haulage level, established over 20 years ago, 250 ft. below the collar of the Humboldt shaft, has above it almost 70 per cent. of the present reserve of the district.

### EARLY HISTORY OF DISTRICT

The early history of the Clifton-Morenci-Metcalf district is closely linked with that of Silver City, N. M., which was founded in 1870 and was originally called San Vicente. Before that time, there was a military post at Fort Bayard, 9 mi. away. Among the pioneer prospectors of San Vicente were some who had been in the Clifton district before 1870 and who had discovered gravel in "Gold Gulch," a tributary to the Eagle Creek, which paid 50 c. to the pan.

The Arizona Central, the first claim in the district, was located in February, 1870, by a party of these prospectors. In July, 1870, a party of 46 men was organized in Silver City and set out for Gold Gulch, some on foot and some on burros, all carrying tools, and heavily armed to defend themselves against the Apaches. They established camp on Eagle Creek to wait for the summer rains, as Gold Gulch was dry. After waiting vainly for four weeks, shortage of food compelled them to return to Silver City, where they disbanded. Included in this party were Ike N. Stevens, now of Clifton, Ariz., and the late Bob Metcalf.

Enactment of the Federal Mining Law in May, 1872, created great activity among prospectors, and at once a party of eight men, including Jim Bullard and Joe Yankie, set out from Silver City and located three

additional claims in this district on the site of the present town of Morenci. These claims were the Montezuma, Copper Mountain and Yankie. While this location work was in progress, a second party started out from Silver City, in which were Captain Joy, sent by Mr. Ward of Detroit, Mich., and I. N. Stevens, to do the necessary work on the four claims, for patent. At almost the same time, a third party left, headed by Bob Metcalf and "staked" by the Lesinskys, merchants of Las Cruces, N. M. This party located ground in the vicinity of the site of Metcalf and then located the Longfellow mine at Morenci.

A meeting was next called of all the men in the district, and the Copper Mountain Mining District was formed in August, 1872, with Joseph Yankie as the first District Recorder. This was then a part of Yavapai County, and the original locations were recorded at Prescott, the county seat.

The Lesinskys put up the capital to build the first "adobe" furnace, which was erected on Chase Creek, below the foot of the present Longfellow incline, in 1873. The concern was known first as the Francisco Mining Co.; later as the Longfellow Mining Co. Charcoal was used as fuel, and the ore was packed down steep trails on burros, from the Longfellow mine, about 900 ft. higher than the furnace. This location proved unsatisfactory, so, later in 1873, a second adobe furnace was erected at the junction of Chase Creek and the San Francisco River, where the town of Clifton now lies. A wagon road was built to the mines at Morenci and water was hauled up and ore was hauled down. A ditch, up the San Francisco River, supplied water power to operate a fan for the blast for the furnace. Supplies were hauled in, and copper was taken out by ox-teams, via Silver City, from Independence, Kans., and later from La Junta, Colo. and Las Vegas, N. M., these places being terminals of the Atchison Topeka & Santa Fe Ry., as it was built westward.

In 1874, a disagreement occurred between the Lesinskys and Bob Metcalf. After some trouble, Metcalf acquired possession of Metcalf Hill, and the Lesinskys of the Longfellow mines. The Lesinskys operated for many years with indifferent success, for added to their financial difficulties were the depredations of marauding bands of Apache Indians.

#### FIRST RAILROAD IN ARIZONA

During this time the ore from the Longfellow mine was hauled by wagon to the Smelter at Clifton, at a cost of \$10 per ton. The Lesinskys, recognizing the magnitude of the deposits, determined to construct the first railroad built in Arizona, in order to reduce the cost of hauling the ore. This road was built during 1878 and the early part of 1879, along the bed of Chase Creek from Clifton to a point below the Longfellow mine. At the same time, a gravity incline, in two separate sections, was built from the mine down to Chase Creek, 900 ft. below; the ore was carried down

the incline in cars and the cars were sent over the new railroad, without unloading. The railroad was  $4\frac{1}{2}$  mi. long, with grades ranging from 2.5 to 5 per cent.

The engineer of construction was Capt. Nicholas S. Davis, who was also engineer at the mines, and he was assisted by Mr. Unthank. Captain

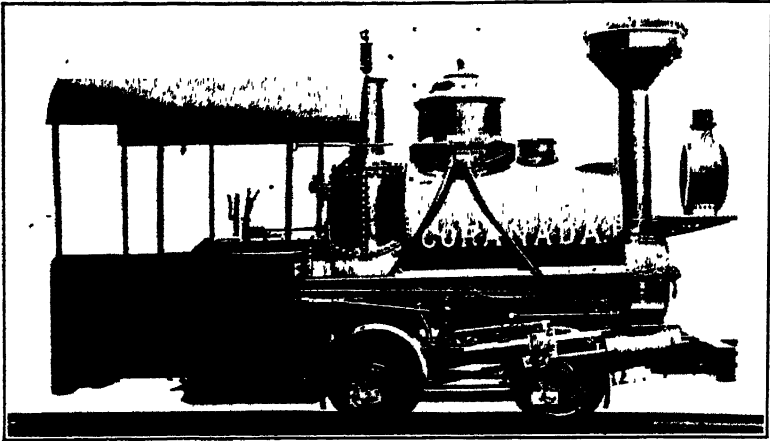


FIG. 2.—FIRST INDUSTRIAL LOCOMOTIVE IN ARIZONA. (PHOTOGRAPH FURNISHED BY H. K. PORTER Co.)



FIG. 3.—PORTION OF ROADBED OF FIRST RAILWAY IN ARIZONA (WHERE MAN IS STANDING) BELOW THE PRESENT CORONADO RAILROAD.

Davis belonged to the California Column during the Civil War, and before the war had worked in mines in California, and it was this experience that led him to adopt a track gage of 20 in., with which he was familiar.

There were no tracks underground in any of the mines, all the ore being removed by wheelbarrows, but later on the underground track was laid on 20-in. gage to conform to that already existing on the surface railroad and inclines. Mules were the first motive power, but they were not satisfactory and a locomotive, Fig. 2, for this work was ordered from the H. K. Porter Co.; the records of that company show that this locomotive was shipped in April of 1880, by steamer around the Horn from New York City to San Francisco. From San Francisco, the only route open for freight at that time was by rail to Fort Yuma and thence to Clifton by ox-team, the route unquestionably followed by this locomotive, which arrived at its destination in the fall of the same year.

The engine had cylinders 6 in. in diameter by 10 in. long; saddle tank; 20-in. gage; and four 22-in. chilled-tread driving wheels. It used wood for fuel. The shipping weight was four tons, and in working order it weighed 13,000 lb.

An interesting item in the Porter company's records is the memorandum that this locomotive was to "have an injector," a new departure at that time. It was also provided with a crosshead pump. It was built to haul 10 empty cars weighing 2800 lb. each, on a 4.5 per cent. maximum grade with 90-ft. radius curves and 16-lb. rails. It was lettered the "Coranada" by the manufacturers, but it was re-lettered in later years and called the "Little Emma."

As soon as the railroad was completed from Clifton as far as Longfellow, the work of extending it up Chase Creek to the Metcalf mines was undertaken. A portion of this original roadbed, below the present Coronado railroad, is shown in Fig. 3.

#### DETROIT COPPER MINING CO.

In January, 1875, William Church, assisted by his brother John, acquired the four original claims of the district from the Ward Estate, and organized the Detroit Copper Mining Co. In 1880, this company built a small smelter on the Frisco River about 3 mi. below Clifton. All the ore was hauled down from the mines to the smelter by wagon. Two years later the smelter was removed to Morenci. In 1887, the Phelps Dodge Co. bought the property from Mr. Church. Until 1901, all incoming supplies and outgoing copper were shipped via the Longfellow incline, over the baby gage to and from Clifton. In that year, the Morenci Southern, a narrow-gage railroad, was completed from Guthrie, on the Arizona & New Mexico R. R., to Morenci, a distance of 18 mi. This road was laid with 50-lb. steel. There was a maximum grade of 3.5 per cent. on tangents and a maximum curvature of 40°. The unique feature of this construction was a series of five complete loops, one by the use of a tunnel near the San Francisco River and four by the use of high wooden trestles in a narrow canyon below Morenci.

The total cost of this road was approximately \$28,000 per mile, including equipment.

#### ARIZONA COPPER COMPANY, LTD.

In the late fall of 1880, the Southern Pacific Ry., being constructed from the west, reached Lordsburg, N. M.

In 1882, the Arizona Copper Co. Ltd., of Edinburgh, Scotland, purchased the mines of the Lesinskys and Bob Metcalf. To provide adequate transportation facilities for the district, so that serious development could be undertaken, the company built a 3-ft. gage railroad from Lordsburg to Clifton, a distance of 70 mi. This road, built in 1883 and 1884, was originally named the Clifton and Southern Pacific, but later was changed to the Arizona & New Mexico. It was laid with 48-lb. and 50-lb. steel. This railway was later extended up to the Longfellow incline, replacing that portion of the original baby-gage line, the extension being completed in August, 1901. Bins at the foot of the Longfellow incline were used for about one year to transfer the Metcalf ore brought down to this point on the 20-in. road. After this time, the change to 36 in. was completed to Metcalf.

The next step forward was taken in 1900 and 1901, when the Arizona & New Mexico was widened to standard gage, the light steel being replaced with 60-lb. and 75-lb. As the light steel was taken up from the Clifton & Metcalf railway (now called the Coronado R. R.) and the main line of the A. & N. M., it was used on the main haulage roads around the mines, which is the reason that the electric haulage system to be described later is entirely laid with 48- and 50-lb. steel rails.

#### SHANNON COPPER CO.

The Shannon Copper Co. was organized in November, 1899, with mines at Metcalf, Ariz. Previous to 1910, ore and supplies were hauled between Metcalf and Clifton by the Coronado R. R. of the Arizona Copper Co., Ltd. During 1909 and 1910, in order to handle its own ores, the Shannon company constructed the Shannon Arizona Ry., 10 mi. long, at a total cost, including equipment, of approximately \$60,000 per mile. The road was laid with 75-lb. steel.

#### DEVELOPMENT OF STEAM LOCOMOTIVES AND CARS

As the mines of both companies became greatly extended and began to work lower grade ores requiring concentration, it became necessary to handle larger quantities of ore and supplies. Mules were largely replaced by steam locomotives and many miles of surface tracks were laid in the district, especially at Morenci and Coronado. Grades of from 4 per cent. to as much as 7.5 per cent. were in vogue. To meet these conditions, the size and weight of the steam locomotives were steadily increased.

Since the arrival of the first tiny locomotive described, sixteen of these 20-in. gage engines have been purchased for this district, all manufactured by the H. K. Porter Co. The last two, supplied to the Detroit Copper Co., show what remarkable performance can be secured on so small a gage. The specifications of these locomotives are: Piston diameter, 11 in.; stroke, 16 in.; driving wheel, 30 in.; wheel base, 5 ft. 3 in.; length overall, 18 ft. 6 in.; height overall, 10 ft. 9 in.; weight as originally supplied, 37,000 lb.; present weight, with cast-iron bumpers added back and front, 40,000 lb.; tractive force, 7540 lb. These locomotives as originally

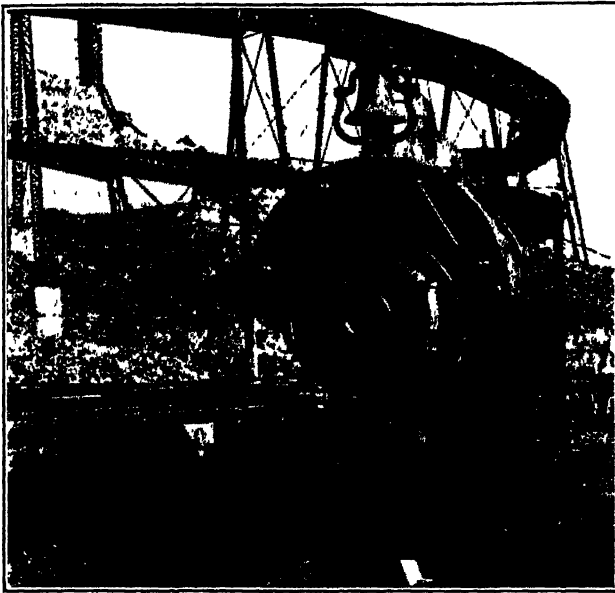


FIG. 4.—A 20-TON LOCOMOTIVE ON A 20-IN. GAGE.

supplied were coal burning but they were later converted to oil burners. These engines have large "overhang," see Fig. 4, but in spite of that fact derailments are rare.

All the earlier cars were of the "rocker" type, the body resting upon half circles of angle iron by which they could be dumped to either side. When underground mining began to exceed in importance the surface mining, the type of car was changed to that of the inverted V-bottom variety with dumping doors along both sides. These were of  $3\frac{1}{2}$ -ton capacity at first, but later were increased to  $4\frac{1}{2}$ ,  $5\frac{1}{2}$  and finally to 10 tons.

#### INTRODUCTION OF ELECTRIC HAULAGE

On main haulage levels, mules were generally used underground, and in some cases still are. In 1905, the Arizona Copper Co. replaced mules



by electric locomotives on the surface and important levels of the Humbolt mine. The heavy grades on the surface roads of the company's property at Morenci were eliminated in 1906. The locomotives were

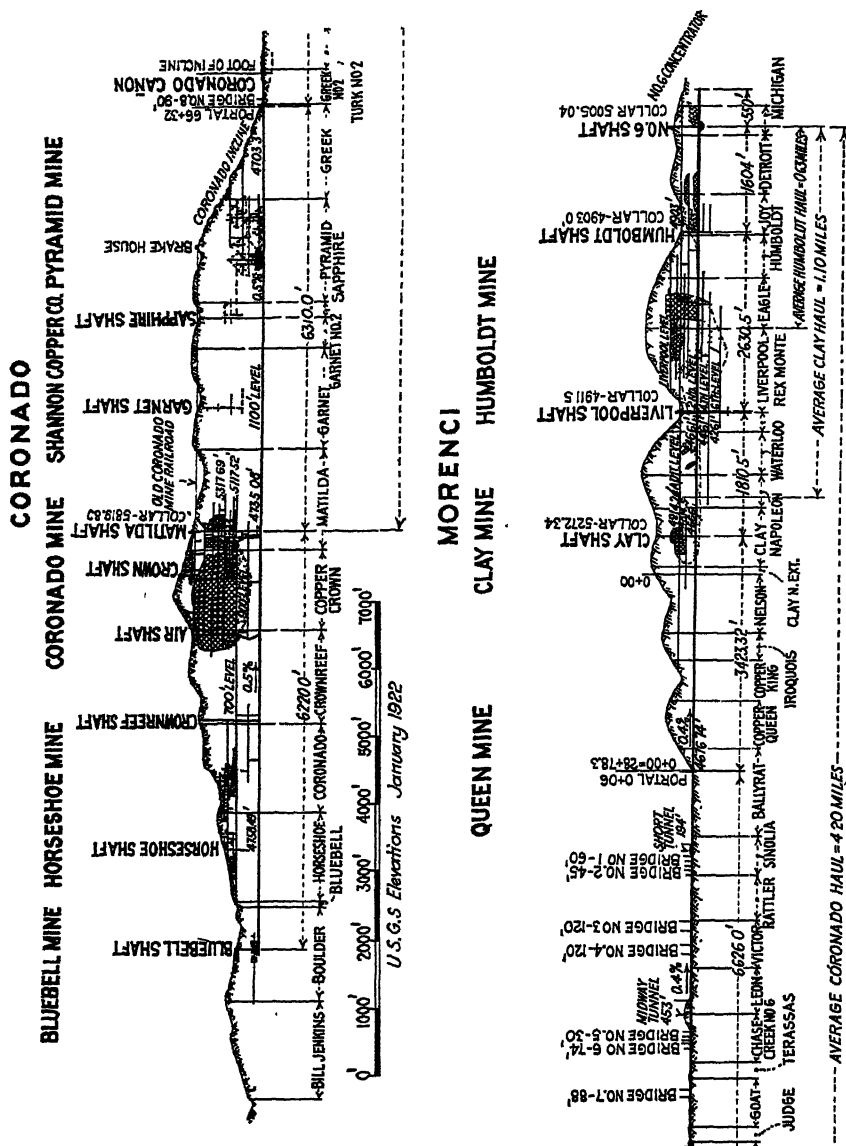


FIG. 5.—LONGITUDINAL SECTION ALONG ELECTRIC HAULAGE ROAD, SHOWING LOCATION OF PRINCIPAL OREBODIES.

furnished by the Jeffrey Manufacturing Co., the first type being a single 6-ton unit, cast-iron frame with 220-volt motors. The driving wheels were of chilled cast iron; each 6-ton unit was equipped with two 15-hp. series motors and had a rated drawbar pull of 1500 lb. at 8 mi. per hour;

the brakes were hand operated. These motors, though now rather small, are still giving excellent satisfaction on surface after 16 years of continuous service.

During the period from 1905 to 1913, the haulage of ore from the Humboldt mine, now the largest producer, to the concentrator at Morenci was performed entirely by electric motors and cars of  $3\frac{1}{2}$ ,  $4\frac{1}{2}$  and  $5\frac{1}{2}$  tons capacity. Previous to 1913, the Coronado mine was quite isolated and the output was handled as follows: A shaft 700-ft. deep, the Matilda, connected the various working levels; through which the ore was hoisted in 1-ton cars to surface and dumped into bins. From these bins it was transferred to a baby-gage steam railway a mile long and delivered to the top of the Coronado incline, which was 3300 ft. long with 1100 ft. difference in elevation between head and foot. Over this incline it was lowered and dumped into bins; another 20-in. gage steam train conveyed the ore to bins on the Coronado R.R. and from there it was hauled to Clifton, a distance of 7 mi., and delivered to a concentrator.

Plans had been laid for changing all this and for connecting the Coronado mine with the Humboldt transportation system through an extension of the electric haulage. These plans called for (a) driving a 3000-ft. tunnel from the Clay mine to daylight (in driving this 8- by 9-ft. heading, a speed of 799 ft. in 31 consecutive days was attained<sup>2</sup>); (b) driving an adit tunnel 5000 ft. from surface into the Coronado mine; (c) connecting these two pieces of work by an outside track, skirting along the hill for 6600 ft.; and (d) sinking the Coronado shaft 400 ft. deeper to connect with this new level. Fig. 5 shows a section along the electric haulage road, which illustrates this piece of work.

In solving this problem, the question of gage was again carefully considered; *i. e.*, whether to continue the use of the present 20-in. system or to adopt the 36-in. gage. It was finally decided to develop the present 20-in. system so as to procure as nearly as possible the same costs as with the 36-in. track and heavier equipment, for the following reasons:

1. The entire haulage system of the Humboldt mine was already 20-in., of which the extension would form but a part. The adoption of a different gage requiring either a three-rail system underground or the changing of the existing elaborate system including tunnels, tracks, chutes, and all accessories, involved an enormous installation cost.

2. The difficulty of supporting ground in the case of such large openings as a 3-ft.-gage track would necessitate.

Fig. 5 shows where the ore is mined and hoisted, also the location of the principal orebodies under present consideration. Mining operations are carried on above the Humboldt second level and above its extension into the Coronado mountain, called the 1100-ft. level. The Coronado

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<sup>2</sup> *Eng. & Min. Jnl.* (Aug. 17, 1912).

ore is transferred by electric haulage in  $3\frac{1}{2}$ -ton cars on the 700-ft. level to ore chutes which deliver it to the 10-ton haulage system. Similarly, a part of the Humboldt ore mined above the adit level is transferred on the adit level in  $5\frac{1}{2}$ -ton cars with electric motors and dumped to the main haulageway 250 ft. below. On the second level of the Humboldt, the ore is loaded from chutes, weighed on platform scales and dumped into two sets of pockets at the No. 6 hoisting shaft. The combined capacity of these pockets is 2300 tons. It is hoisted in 5-ton skips from a point in the shaft 80 ft. below the haulage level into a 1000-ton mill bin. The capacity of the concentrator is 4000 tons per day.

### LOCOMOTIVES FOR 300-TON TRAIN

The problem of building the most powerful locomotive for the 20-in. gage was then submitted to the makers, but their only suggestion was to change the tires from chilled iron to steel to increase the tractive effort or to couple two locomotives of two units each with two controls, requiring two operators and making a tractor 50 ft. long. This was not satisfactory, and finally our own electrician devised a means of coupling three units. The three coupled units had a single control composed of two controllers placed one above the other and operated from the same lever which gave a tractor with an approximate drawbar pull of 10,000 lb. The wiring was brought out symmetrically to a terminal block and connected with jumpers so that the third unit could be quickly uncoupled.

An oversize compressor was installed for the 10-ton haulage train, requiring a larger air receiver and a triple air valve. On the third, or replaceable, unit the original controller and pantagraph was left to operate in case of emergency. Locomotives supplied by the Jeffrey Manufacturing Co. for this heavy service were equipped with driving motors increased in size from 15 to 30 hp., which is the largest motor that can be placed between the driving wheels. Steel-tired wheels were substituted for chilled-cast ones. The entire locomotive equipment, totaling 23 single units, has been furnished by the Jeffrey Manufacturing Co.

The general specifications and dimensions of these triple-head locomotives were as follows:

Weight.....	18 tons
Volts.....	250
Number of motors.....	6
Control.....	Center
Wheels.....	Inside
Rated drawbar pull.....	9000 lb.
Starting drawbar pull.....	10,000 lb.
Miles per hour at full load speed.....	6
Track gage .....	20 in.
Overall width .....	40.5 in.

Length of frame for each unit . . . . .	11 ft. 3 in.
Height of frame above rail.....	37 in.
Height over cover.....	48 in.
Maximum overall height above rail with trolley pole locked down.....	55 in.
Wheel base.....	42 in.
Diameter steel-tired wheels . . . . .	26 in.
Frame.....	structural steel
Trolley . . . . .	diamond type

### DEVELOPMENT OF 10-TON CAR

The next step was to provide the largest car that could be operated on track of this gage. A 10-ton car supplied by the manufacturers could



FIG. 6.—ONE-TON, 5½-TON AND 10-TON CARS ON 20-IN. GAGE.

not be operated except on a perfectly straight track. The entire truck and draft rig was redesigned and rebuilt in our own shops, air brakes were added to one-half of the cars, and the other half were equipped with train pipes. To show the relative size of this car, the following comparisons are given (see also Fig. 6):

	3¼-Ton	5½-Ton	10-Ton
Capacity.....	65 cu. ft.	110 cu. ft.	200 cu. ft.
Wheels C. I. diam.....	24"	24"	24"
Length inside....	8' 0"	8' 0"	11' 6"
Width.....	4' 6"	5' 8"	5' 10"
Overall length.....	11' 4"	11' 4"	14' 6"
Height above rail.....	4' 9½"	5' 3"	5' 8½"
Coupler height.....	25"	25"	17"
Wheel base.....	4' 0"	4' 0"	5' 0"
Underframe channels.....	7"	7"	8"
Thickness of body plates.....	¼"	¼"	⅜"
Journals.....	3¾"×5½"	3¾"×7½"	4½"×7½"
Weight-empty.....	5500 lb.	7000 lb.	9700 lb.

Cars are all steel construction and are of one general type; namely, gable bottomed, side dumping. In all cases the journal bearings are of M. C. B. type, outside the wheels, with suitable double-coil springs over the journal boxings. All cars have full length doors, each of which is swung by three or four hinges and held by a like number of catches or dogs on a through horizontal square rod. This in turn is operated by a hand lever at one end of the car, fastened by a slip link. All cars are provided with standard-design double-coil spring draft gear. Couplers on the  $3\frac{1}{2}$ - and  $5\frac{1}{2}$ -ton cars are of malleable cast iron, to take links and pins; on the 10-ton cars, M. C. B. standard automatic couplers of three-quarter size are used. The difference of 8 in. in the coupler heights between the 10-ton and the smaller cars, as given in the table, calls for special connecting bar. For the same reason, the locomotives are provided either with a special double-mouthed drawhead or with two single drawheads, one placed immediately above the other.

The 10-ton cars, as originally supplied, were equipped with Hyatt spiral roller bearings between the wheels. Rollers were 6 in. long and were used with a 3-in. diameter axle. Wheels were ribbed single-plate type, one tight and one loose. No springs were provided, the axle housings being bolted rigidly to the body channels. This general design proved unsatisfactory, and was changed at once to provide bearings outside of the wheels, as already noted.

The single-plate wheels were not strong enough to stand up under the load, and the double-plate type was substituted. The latter wheel has proved entirely satisfactory. To take the wear of the follower plates in the draft gear of the 10-ton cars and to prevent the consequent failure of the 8-in. body channels,  $\frac{1}{4}$ -in. replaceable wearing plates of scrap material are now used. Hand brakes of regulation type are used on all surface cars, but underground no hand brakes are used. The air-brake equipment for one 10-ton car, as supplied by the Westinghouse Air Brake Co., consists of:

- 1 Type D, 6- by 8-in. brake cylinder
- 1 Type D, auxiliary reservoir
- 1 H. I. triple valve
- 1 Release valve complete
- 1 Cut-out cock
- 2 Self-locking angle cocks, 1 by  $1\frac{1}{4}$  in.
- 2  $1\frac{1}{8}$ - by  $\frac{1}{8}$ -in. hose with F. P. 4 couplings.

#### COLLECTOR SYSTEM

All trolley wire over surface track is 00, figure eight, copper. On surface, this wire is maintained at a height of 9 ft. and supported by standard flexible brackets and cross-span construction, as developed for similar traction systems. Underground, Section 35 of the Arizona State Mining Code provides that "electric trolley wires in all mines now (1912)

equipped with same shall be at least  $6\frac{1}{2}$  ft. above the floor. In all mines hereafter so equipped, at least 7 ft. above the floor." Tunnel sections for both timbered and untimbered motor tunnels have been standardized since the passage of the above law and are shown in Figs. 7 and 8. The height of the trolley in these sections is 7 ft. 5 in. and 7 ft. 10 in. respectively.

At first, the practice was to use rigid barn hangers, but it was found that occasional high peaks of ore bent the trolley wire upward on both sides of the hanger, and the resulting kinks seriously interfered with the operation of the collectors, besides causing bad burning from the excessive sparking at those points. To meet these difficulties, flexible supports

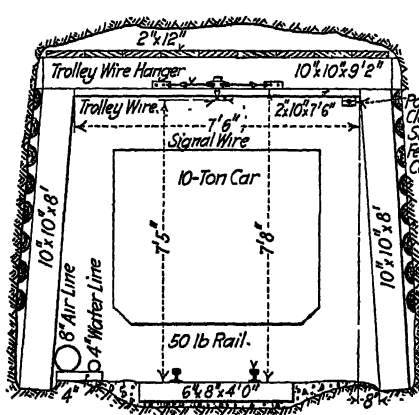


FIG. 7.—CROSS-SECTION OF TIMBERED TUNNEL.

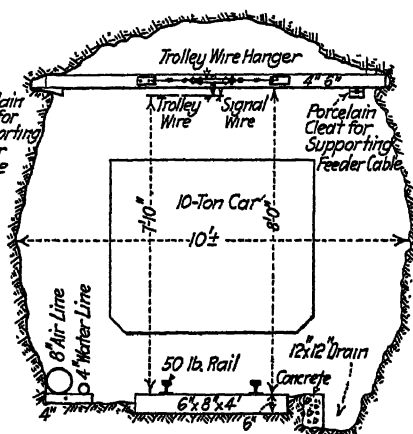


FIG. 8.—CROSS-SECTION OF UNTIMBERED TUNNEL.

have been adopted. Several different types of these supports have been installed and tried out on the various underground roads, and two have been selected as best fitting our requirements. One is the straight-line suspension made by the General Electric Co., Form H, consisting of a straight-line hanger and trolley ear carried by a  $\frac{5}{16}$ -in. guy wire, see Fig. 7. This support is used on straight trolley lines, where it gives excellent satisfaction. On curves, however, the center piece will shift and cause trouble, therefore a second, more expensive type is used for curves. This is a straight-line suspension with composition strain insulators carried in the same manner as the first one described, see Fig. 9.

In ground where timbers are moving, the trolley wire difficulty is taken care of by frequently dead-ending both ways with the ends overlapping for a distance of about 5 feet.

All electric locomotives are provided with diamond or pantagraph type of collectors. A slide has been tried instead of the roller, but was discarded after a short trial because of increased trouble from panta-

graph breakage. This slide, mounted at the top of the pantagraph, consisted of a sheet base carrying two copper collecting strips on its top with a channel between to hold grease for lubrication. The type used

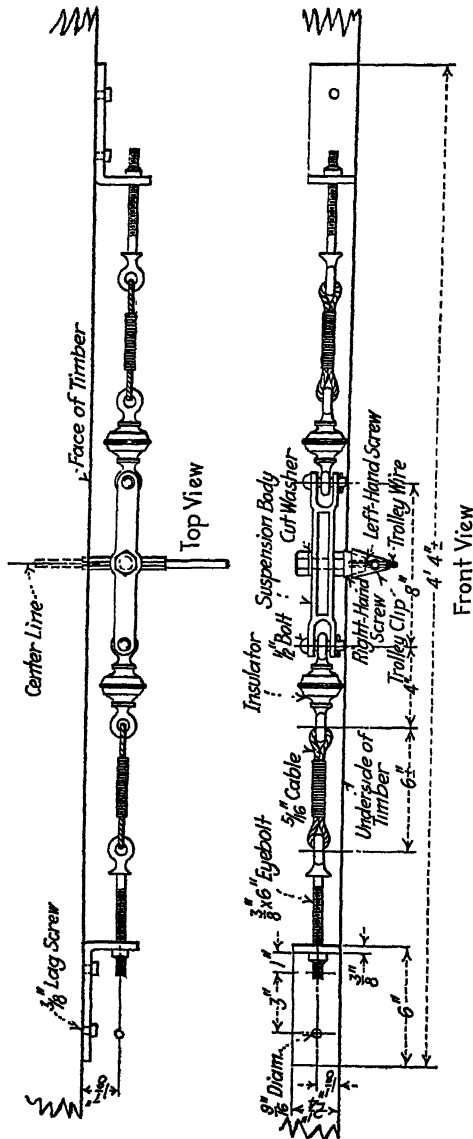


Fig. 9.—FLEXIBLE TROLLEY HANGER.

now is shown in Fig. 10. This pantagraph is much more rigid than the first type used, and the roller rarely slips off the trolley wire. The first type consisted of four members or legs in a single plane; with this construction, the wooden sticks are the weakest members, and if the panta-





ways are laid with 35- or 25-lb. steel, bonded with 2/0 bonds of similar type. Temporary tracks are laid with 25-lb. steel and bonded either with channel pins and 2/0 solid annealed copper wire, or with removable flexible bonds with tapered steel pins. To facilitate inspection, all bonds are exposed, the holes for the terminals being placed outside of the splice plates, 29 in. apart, with the bond itself measuring 32 in. in length. These types of bonds are used because they can be installed by unskilled labor. In addition to the regular rail bonding, all tracks are crossbonded between the two rails. The haulage-track systems on the adit and second level are tied together, through the Humboldt shaft, by two 500,000-cm. cables, and a second tie is to be installed through the Liverpool shaft. From these Humboldt shaft cables and the adit level track system, four return conductors of 4/0 bare copper wire go to the negative bus on the d.c. switchboard. All rails on the adit level, for several hundred feet in both directions from the point of taking off this return, are double bonded. At the Coronado adit, the return current is conducted in a similar manner, to the Coronado sub-station panel.

Underground haulage tracks are laid with 6- by 8-in. ties, 4 ft. long, spaced 30-in. centers. On surface, the ties are also 6 by 8 in., spaced 30 in., but are 5 ft. in length. Spikes 5 in. long are used throughout.

Grades in the old parts of the mine, though somewhat variable, as a rule are not over 0.5 per cent. The maximum for the old portion of the second level haulageway is 0.9 per cent., which occurs just north of the Humboldt shaft for a distance of only 450 ft. In all tunnels driven since the adoption of the electric haulage, a grade of 0.4 per cent. in favor of the load has been maintained. Experience has shown that slightly less grade would more nearly equalize the drawbar pull for the loaded and empty trains. Curves of 100-ft. radius have been installed in all recent work, where it is possible to do so. For the 10-ton car haulage, the minimum curve has an 80-ft. radius, and for the 5½-ton car haulage, a 40-ft. radius.

For the 50-lb. rails, stiff bolted frogs are used with cast-iron spacing blocks. These frogs are constructed of standard steel, except on the second level haulageway, where a number of frogs with manganese steel inserts have been installed. The insert is a one-piece casting designed to give a full tread bearing over the area of maximum wear. The cost of these frogs was from two and a half to three times greater than that of the regular frog, but present indications are that they will be cheaper in the end. Frogs for the lighter rails are partly of the above type and partly those riveted on steel plates.

Split switches are used very generally on the 50-lb. tracks, both surface and underground, but stub switches are used around loading chutes and other points which are very difficult to keep clean. Stub switches are also used for the lighter rails.

The form of switch stand commonly used is an inexpensive one of the ground-throw type, provided with either plain or weighted lever, which operates at right angles to the track. The weights are provided with a handle to facilitate the throwing. In recent years, stands with the throw parallel to the track have been tried out and are considered more satisfactory, as there is less liability to accident in operating them.

### SWITCH AND BLOCK SIGNALS

All underground track switches are provided with signal lights, which show the position of the switch. Green lights indicate that the main trunk line is clear; red, that the switch is set for some branch or siding

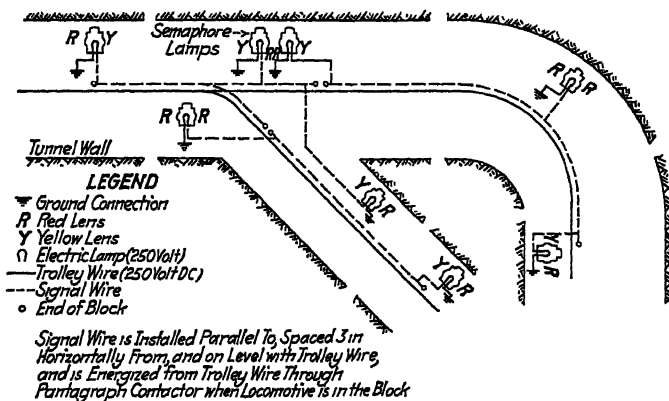


FIG. 11.—DIAGRAMMATIC SKETCH OF WIRING FOR BLOCK SIGNAL SYSTEM

off the main line. This is accomplished by means of a double-throw electric switch controlled by the track-switch operating mechanism, actuating the negative side of the wires from the colored lamps which are connected to the trolley circuit.

A block signal system has been devised and installed underground and on the dangerous curves on the surface lines. This installation consists of a separate signal wire of No. 2 hard drawn copper, paralleling and 3 in. away from the trolley wire. When the locomotive is in the block, the 20-in. copper roller on the pantograph bridges these two wires, impressing trolley voltage on the signal wire and thereby lighting 25-watt, mill-type lamps in semaphore lanterns at both ends of the block and on the curves. These lamps are all placed on the same side of the tunnel and on the same side as the switch lights. The lamps are connected to ground. Red and yellow lenses are used on the lanterns, which have two globes in parallel, thus insuring a signal even though one globe burns out. The accompanying diagrammatic sketch, Fig. 11, shows the operation on a straight track, on a curve, and in a side drift. The lamps on curves can be seen from either direction. They are installed



spotting. The two regular brakemen attached to the train operate the chute doors from the top of the platform.

### SOURCE OF POWER

Power for all of the various operations is generated at the power plant situated at the smelter in South Clifton. The installation consists of three 2000-kw. Curtiss type, 1800-r.p.m. steam turbines, direct connected to 2500-kv.-a., 6600-volt, three-phase, 60-cycle, General Electric generators, each of which is direct connected to three 417-kv.-a. 6600- to 13,200-volt star connected auto transformers. Steam at 170-lb. gage and 75° superheat is supplied by five Sterling boilers of 713 hp. fired by waste heat from two 22- by 100-ft. reverberatory furnaces, also three 713-hp. and three 384-hp. Sterling boilers, oil fired. Under normal operating conditions, an average of 4000 kw. electric power is required for smelting, concentrating, mining and miscellaneous company operations. Of this total, the average consumption for electric haulage at the mines, both surface and underground, is from 2 to 2.5 per cent., and the peak load for the haulage is about 5 per cent. of the powerhouse peak.

### HIGH TENSION TRANSMISSION

Power is transmitted from central power plant to sub-stations at 13,200 volts, three-phase, over two circuits of No. 2/0 B. & S.-gage standard copper cable carried on "Tripartite" steel poles with pin insulators, to No. 6 mill sub-station, a distance of 5 mi., and then over two circuits of No. 4 B. & S.-gage stranded copper cable in "Tripartite" steel poles to Coronado sub-station, a distance of  $2\frac{1}{4}$  miles.

### *Sub-stations*

There are three sub-stations, located respectively at No. 6 concentrator, at the Humboldt adit and at the Coronado adit. All power for No. 6 mill is passed through the No. 6 sub-station, which, in addition, delivers all current for Longfellow division mining purposes at 2300 volts, three-phase, to the Humboldt adit sub-station, over a single 250,000-cm. circuit. At this station are situated two large synchronous motor-driven air compressors and two 300-kw. rotary converters, one used at a time, which supply all direct current for haulage and other purposes. Similarly, at the Coronado adit sub-stations there are two smaller compressors, one driven by a synchronous motor and one by an induction motor, and two 150-kw. rotary converters furnishing direct current for underground and surface haulage in the Coronado mining division. A 2300-volt surface line from this station to the Matilda shaft hoist supplies a 150-kw. rotary converter, which in turn supplies power to operate the Matilda hoist, and for the Coronado mine.

*Distribution of Power from Sub-station*

For reasons of economy and convenience of operating, the surface and underground roads are sectionalized or divided into separate units, depending on their location or on their duties, which may change on any of the three different shifts. In this way the current is cut off from any section in which the particular work of that section has been finished for the day. There are six of these sections at the Longfellow division and two at the Coronado. Each section is served by separate 250-volt feeder circuits direct from the sub-station. These lines are of 500,000-cm. triple-braid weatherproof cable, and each is provided with an 800-amp. circuit breaker and a 450-amp. watt-hour meter at the sub-station. In addition to the needs of the haulage system, there are numerous direct-current motors, lights, etc., in each section.

The current to each section is generally tapped into the trolley lines at a point nearest the sub-station. In the case of some of the smaller sections, no additional feeding is needed, but in the larger ones the main feeder is extended to parallel the trolley line along the main haulage artery and the potential is kept up by tapping over to the trolley wire at intervals of from 350 to 750 ft., as best suits the particular loads and duties within the section. For example, the second level haulage of the Humboldt mine is connected up as follows: Two 500,000-cm. weatherproof cables are taken from the Humboldt adit down the Humboldt shaft to the second level. At the foot of the shaft they are connected through three switches into the three sections comprising this level. One main feeder of 500,000-cm. cable, from this point, parallels the main Humboldt, Clay and Coronado haulageway, from which taps are taken off the trolley wire at average intervals of 500 feet.

A second example is that of the Coronado adit. This unit is served by a 750,000-cm. circuit from the Coronado sub-station tapped to the trolley wire at the portal. From this point a 500,000-cm. feeder 6500 ft. long parallels the trolley line to the bottom of the Matilda shaft. A second feeder of 500,000 cm. from the Matilda shaft hoist house is strung down the shaft. As this shaft is very wet with strong copper water, the cable used has varnished cambric insulation, lead covered, steel wire armor and jute cover, all kept well painted. This feeder is 1300 ft. long and is tapped on the 700-ft. level for the transfer electric haulage and 50-hp. motor-driven ventilating fan, and is connected through a 600-amp. carbon break circuit breaker to the 1100-ft. adit level feeder.

The surface roads at Coronado are paralleled by two 6500-ft. 4/0 bare feeders to the Queen adit, which is the junction point between the Coronado and Longfellow systems. At this point the two haulage systems are tied together through a 300-amp. automatic reclosing circuit breaker, arranged to open automatically in case of trouble on either end, and to

remain open until the trouble is corrected. With this tie between feeders, a locomotive working in the neighborhood of the junction point gets the benefit of feeders from each direction, which results in materially improved voltage regulation.

Under curtailment conditions, it has been possible with this device to shut down the Coronado adit sub-station and to operate the second-level haulage with the rotaries at the Humboldt and Matilda shafts, 21,500 ft. apart. The voltage drop, though considerable under these conditions, is not sufficient to cause trouble in operating; the power loss is less than the station loss of the extra rotary, and there is an additional saving of the operating labor of one sub-station.

### *Power Consumption and Losses*

The power consumption on the different portions of the haulage system varies widely, according to the conditions. On different sections of the surface and adit roads of the Longfellow division, the range is from 0.44 to 2.23 kw.-hr. per wet ton-mile, and on the second level from 0.15 to 0.20 kw.-hr. This large difference in power consumption is due to the fact that on the second level a large tonnage is hauled with a comparatively small amount of switching, empty hauling and miscellaneous work, while on the surface the tonnage handled is comparatively small, with a relatively large amount of handling supplies, switching, running empty, etc.

These consumption figures are based on the d.c. output from the sub-station, and include the distribution loss between converters and electric locomotives, which is 5 to 20 per cent. of the d.c. output, depending on the distance of the locomotive from the sub-station. The transmission losses from the power plant to the rotary converter sub-stations, including step-down transformer losses, under normal loads are 5 to 7 per cent. The sub-station losses of rotary converters and step-down transformers at Longfellow are 15 to 20 per cent.; at Coronado, 20 to 30 per cent. These losses seem high, but are explained by the fact that they operate at an average of only about 25 per cent. of rating. The excess capacity is necessary for peaks, which are relatively high because of the comparatively few operating units.

### *TIME STUDIES*

Time studies are made periodically of the various operations connected with the haulage system. The circle shown in Fig. 13 gives the average results for a month of all operating labor connected with movements of second-level haulage trains. This chart shows the distribution of time on a percentage basis, of the 10-ton haulage, as only 10 per cent. of the total ore is hauled in other than 10-ton cars. Up to the time of this particular study, although the figure for total cost of

train operation for the entire level was correct, the apportionment of this cost among the various mines was being made on an assumed basis. The percentages shown form the basis of a correct distribution of this total cost. Of the items shown, it is assumed that hauling is the only one that is a function of the distance; the items of loading, unloading, and weighing are functions of the tonnage; and the items of switching, miscellaneous and idle, are more nearly functions of the tonnage than of the distance, and have been so considered. Reducing the average haul to 1 mi. instead of 1.07 mi., therefore, affects only the one item of hauling. The percentage time for hauling refigured on a 1-mi. basis is 23 per cent. instead of 24 per cent. as shown. On this basis, the following formulas were developed by J. R. Wester, the foreman of transportation, to apportion

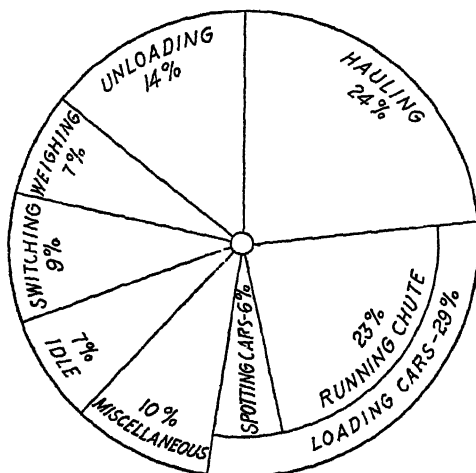


FIG. 13.—TIME DISTRIBUTION COVERING OPERATIONS OF SECOND-LEVEL HAULAGE TRAINS FOR AVERAGE HAUL OF 1.07 MILES.

tion the total cost of train operation for the varying lengths of haul from the principal mines:

$$\text{Cost per wet ton hauled} = C [0.77 \text{ plus } (0.23 \times \text{Distance})]$$

$$\text{Cost per wet ton-mile} = \frac{C}{\text{Distance}} [0.77 + (0.23 \times \text{Distance})]$$

where C is a constant equal to the operating labor cost when the distance is 1 mi. These formulas are shown graphically in Fig. 14.

\* The total haulage cost can be apportioned by the above formulas among the different chutes or mines located at varying distances from the hoisting shaft. The accuracy of the formulas has been proved by keeping a log of the train movements at the scale house near the No. 6 shaft. The costs, apportioned on this "log" basis, checked the same costs as figured by the formulas. In keeping this log, unaccounted-for time was apportioned out at the end of the month among the various

mines on the basis of total hours actually charged to that mine. The cost of train operation includes the labor of the train crew only. As this crew, comprising three men, loads, hauls and dumps the ore, this figure represents the cost of these three operations.

#### COST OF TRANSPORTING WITH 300-TON TRAIN

The costs for the year 1921, prior to suspension of operations, are given below for the transportation of second-class ores from the various mines to the pockets at No. 6 shaft. The costs include loading and dumping, and all expense incidental to haulage, except repairs to the

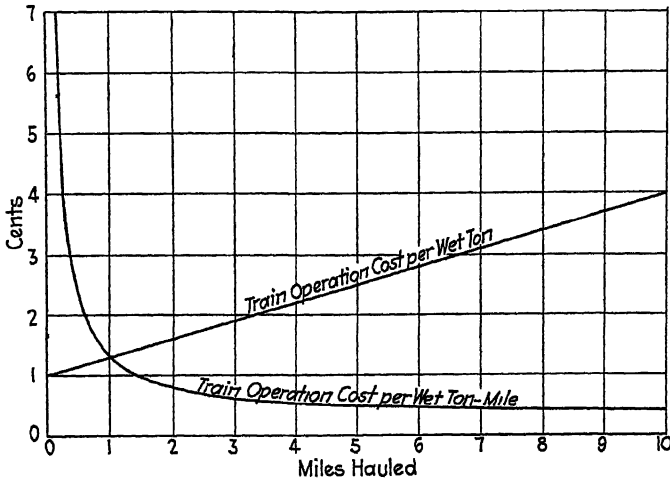


FIG. 14.—COST CURVES OF TRAIN OPERATION, SECOND-LEVEL ELECTRIC HAULAGE.

tunnels and loading chutes, which are considered as items of general mine expense rather than of transportation.

	HUMBOLDT	CLAY	CORONADO
Average daily tonnage (dry).....	2,076	302	301
Average haul in miles.....	0.63	1.10	4.21
<i>Cost per Wet-ton Mile</i>			
Operating train.....	0.0181*	0.0122*	0.0045*
General—including supervision.....	0.0038	0.0028	
Cleaning tracks and blasting chutes.....	0.0048	0.0062	0.0036
Track maintenance.....	0.0067	0.0069	0.0089
Trolley line maintenance.....	0.0024	0.0024	0.0017
Locomotive maintenance.....	0.0032	0.0033	0.0027
Car maintenance.....	0.0050	0.0051	0.0041
Block signal maintenance.....	0.0008	0.0008	0.0007
Power.....	0.0067	0.0069	0.0078
New equipment.....			0.0001
	<hr/> 0.0515	<hr/> 0.0466	<hr/> 0.0341

\* These are the items which are referred to in Figs. 13 and 14.



The average power consumption for the entire second level, corresponding to these cost figures, was 0.20 kw.-hr. per wet ton-mile, measured at the outgoing meter at the sub-stations. The wages in effect during the period recorded were:

Motormen.....	\$5.04 per shift
Brakemen.....	3.80 per shift

#### TRAIN OPERATION AND PERFORMANCE

The regular haulage train consists of thirty 10-ton cars with a "triple-head" Jeffrey locomotive, see Fig. 15. It is operated by a crew of three men; one motorman and two brakemen. This crew loads the train at

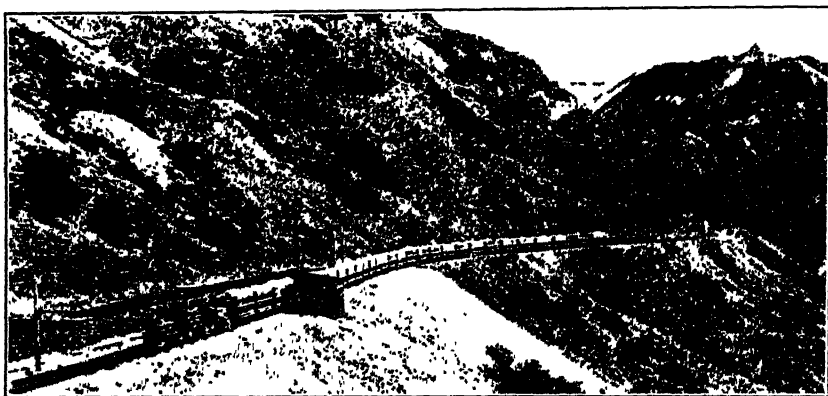


FIG. 15.—A 300-TON TRAIN ON 20-IN. GAGE, SHOWING TRIPLE-HEAD LOCOMOTIVE.

the mine chutes; hauls and dumps the ore at the hoisting pockets. All ore is weighed on a Fairbanks-Morse track scale on the main haulage road, near the hoisting shaft. This scale has a platform 44 ft. long with a capacity of three cars. The weighing is done by a man who also samples the ore in the cars, the cost of which is not charged to the haulage. One miner is used, on the day shift only, for blasting "hung-up" chutes, and a spare brakeman is carried, on the day shift, who does the track cleaning. A blacksmith and helper, on the day shift, make all the necessary car repairs, including those to air-brake equipment, and do the train oiling. One electrician and a helper are employed on the day shift, who do all locomotive repair work and oiling, all track bonding, block and switch signal repairing and upkeep of trolley lines. Track work is done by one head trackman with from one to three laborers. One transportation foreman is employed on the day shift.

A locomotive is never operated continuously for more than 8 hr. The running speed of the train varies from 5 to 7½ mi. per hour. About

1800 tons per shift are hauled from the Humboldt mine with one train. Time studies give the following averages for the Humboldt mine:

	TIME, MINUTES
To load thirty 10-ton cars at mine chutes.....	35
To weigh thirty 10-ton cars at scales.....	7
To dump thirty 10-ton cars at pockets.....	19

On a 0.4 per cent. down grade. the 30-car train, running at a speed of 7 mi. per hour, is stopped by the air brakes in from 20 to 22 seconds, in a distance of from 125 to 145 ft. The voltage drop is not excessive when starting the heavy loaded trains from rest. The average drop is only 22 volts, with a maximum of 32 volts. The average time taken by motormen to cut out all resistance, motors in full parallel, is 40 sec. and the total time of acceleration is 1 min. 45 sec. Arc masters were tried out on the control, but their use has been discontinued.

#### FATAL ACCIDENTS DUE TO ELECTRIC SHOCK

From the installation of the electric haulage in 1906 to the present time, there have been four fatal accidents attributed to contact with either the trolley wire or a feeder wire.

1. In 1908, a brakeman was killed at No. 26 chute on the Humboldt adit. After helping to load a train of  $5\frac{1}{2}$ -ton cars, he jumped down from the overhead loading platform upon the rear of the locomotive, instead of using the ladder provided for this purpose. In doing this, his neck came in contact with the trolley wire. His feet were wet and the shock was instantly fatal.

2. In 1912, two muckers were shoveling up spill along the haulage tracks near No. 28 chute, Humboldt adit, behind a standing  $5\frac{1}{2}$ -ton car. One of these men started to climb over the car to the opposite end and it was thought that his neck came in contact with a bare feeder wire. He fell forward against the edge of the car and sustained a blow over the heart. His death resulted.

3. In 1914, while the shift was coming off at the Coronado mine, a mucker attempted to climb over the end of one of the cars of the train regularly used to haul the men out. The train was standing on a siding near the Matilda shaft and had not yet been switched into its regular place, where a switch cuts the current off the trolley line. His neck came in contact with the live wire and he was instantly killed.

4. In 1915, while driving the Coronado adit heading, a mule driver, whose duty it was to haul  $5\frac{1}{2}$ -ton cars of waste, was found dead. There were no witnesses, but the Coroner's jury decided that he must have stood up on the drawhead and come in contact with the trolley wire. His feet were dry and no marks were found upon his body.

As more effective precautions have been taken and safety devices have been improved, the accident rate has been materially decreased. This is shown by the figures of comparative tonnages handled for the above four fatalities, as follows:

FATALITY No.	DATE	APPROXIMATE TONS HANDLED BY ELECTRIC HAULAGE SYSTEM
1	1908	3,100,000
2	1912	2,068,000
3	1914	1,032,000
4	1915	9,300,000

### ACCIDENT PREVENTION

The underground haulage tunnels are well lighted. All switch and block-signal lights are kept on one side of the tunnel, and on the opposite side is installed a series of white lights. Each white light indicates a place of safety, into which a workman can step to allow a train to pass. These places are spaced about 100 ft. apart. Where possible, existing branch drifts are used but where these are not available special safety holes are constructed. The drifts in the neighborhood of the safety places are whitewashed to afford all possible light. One white light in the back of the drift illuminates each frog and switch. This light is placed so that it cannot be seen from along the haulageway.

The haulage drifts are kept clean to prevent slipping or falling. The open ends of frogs are filled with plank, for the same reason. Electric trolley wires are being gradually brought up to standard height, and bare feeder wires underground have been entirely eliminated. The design of the loading chute has been improved, making it impossible to jump down upon the train from the overhead platform, and removing all reasonable possibility of accidental contact with the trolley wire.

At all points where men, timber, or supplies of any kind are loaded or unloaded, provision is made for cutting off the current in the trolley wire by means of necessary section insulators and single blade switches. When repair work is in progress on the haulage drifts, the trolley line is first "killed."

Electric bells and semaphore arms, operated by the block-signal system, are situated at the mine tunnel portals and at both ends of surface tunnels, to give warning of approaching trains. Solenoid crossing bells with 10-in. gongs are used; the semaphores are made by our own electrical department.

### ACKNOWLEDGMENT

In preparing this article, we wish to acknowledge the assistance rendered by the technical staff of both the Arizona Copper Co. Ltd. and the Phelps Dodge Corp.; by Mr. Ike Stevens, of Clifton, Ariz.; by

the H. K. Porter Co. of Pittsburgh, Pa.; and by Geo. H. Kelly, Arizona State Historian.

#### ADDENDUM

Since the preparation of this article, the properties of the Arizona Copper Co. Ltd. have been merged with those of the Phelps Dodge Corp'n. The merger was completed in December, 1921, and at the same time the Arizona & New Mexico R. R. was transferred to the El Paso & Southwestern system.

#### DISCUSSION

NORMAN CARMICHAEL.—We realized the objections to the gable-bottom car, but were almost forced to its adoption by the same reasons that caused us to retain the 20-in. gage. To use another car would have meant a vast number of changes, for our transportation system was quite extensive; all mine chutes and ore bins were arranged for that car. Had we been laying out new works, many of our decisions would have been different.

MEMBER.—If you were planning it now, would you not put in box-bottom cars with a rotary dump?

NORMAN CARMICHAEL.—We surely would. One objection to the gable-bottom car is the spill. No matter how carefully the cars are kept up, there is always leakage and spill. The cost of keeping and maintaining the cars in a good state of repair, so as to keep that loss at a minimum, is not necessary for a box-bottom car.

CHARLES LEGRAND, Douglas, Ariz.—I am quite familiar with the system and believe the success of the 20-in. gage and the 10-ton car is mostly due to the good heavy track and the trolley construction used. From the statement on p. 838, some people might think that the roller bearing is not a success; I think the trouble was that the car had no springs. A correction of that statement might be fair to the user and maker of roller bearings.

The paper has a most interesting study that is not usually carried out in the mining business—a time study on the running of trains. The importance of having the proper loading system in transportation is shown by the fact that loading at the chute takes 29 per cent. of the total time on a 1 mile haul. If the running time of the locomotive is only 24 per cent. of the total time, possibly a storage-battery locomotive could be used to advantage.

There is no statement as to the cost of installing the trolley system. Knowing such costs would help greatly in determining the merits of the storage-battery locomotives, as compared with trolley locomotives. The trolley has certain dangers in the mine, especially where a high

voltage is used; for which reason, and because of the flexibility of the storage-battery system the costs of installing the trolley system would aid people trying to decide which system to use.

B. B. GOTTSBERGER,\* New Haven, Conn.—At the Calumet & Hecla, on the 5000-ft. level, they have installed one large haulage drift. All ore below that level is hauled to this one, up inclines along the vein, and there delivered to the shaft for hoisting. Storage-battery locomotives are used on all the actual stopping levels, but the trolley system has been adopted for the line on which all the ore is collected together, so that they can run heavy cars and large trains.

NORMAN CARMICHAEL.—The storage-battery locomotive had not been developed to where it was able to compete with the trolley system when this trolley system was inaugurated in our mines. There, again, it was simply a case of extending a system then in use.

It is only fair to the makers of roller bearings to say that the failure of the roller bearings was undoubtedly due to the lack of springs on the first cars, which shows the difficulty we encountered at the time. We wanted a car that would hold 10 tons and run on a 20-in. track, and we could not find it. We put the problem up to the manufacturers who had supplied all our cars up to the 5½-ton size and that was what they gave. It was a failure and we had to design and build the car ourselves.

We also met the same difficulty in connection with the locomotive. We asked the manufacturers to give us a locomotive that would be three times as powerful as the one unit they had supplied. They had already put on the heaviest motors they could place between the wheels on a 20-in. track. They could not, therefore, increase the power by increasing the size of the motor, nor could they design a control that would enable us to run a three-unit locomotive with one man, which we insisted upon. All they could suggest was to change the tires from chilled iron to steel to increase the tractive force. They sent us such a locomotive, but it was not powerful enough. Our electrician finally designed a control for a three-unit system, which enables us to operate a triple-headed locomotive with one engineer; we have been using this ever since.

The weight and the solidity of the roadbed has been mentioned. We found that using heavy steel, heavy ties, and good construction cut down the loss of time through bad tracks and the cost of maintaining bad tracks.

We had one advantage, however. Our standard-gage railroad, 70 miles long, to Lordsburg, had been laid originally with 50-lb. steel rails. When they became too light for the standard-gage railway and had to be taken up, we used them on our electric haulage lines, both underground and on surface. To make the track as solid as possible we used 6 by 8 in.

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\*Professor, Mining Engineering, Yale University.

ties (the same size we used on the main lines) and have found it paid to do so. The table, on p. 849, shows the effect of all the means taken to obtain satisfactory results.

JOHN KIDDIE (written discussion).—Answering Mr. Le Grand's query: the cost of installing a trolley system would differ somewhat, of course, under different conditions, but the following are considered representative here for the system described:

	PER FOOT OF DRIFT
Trolley line (including supporting stulls).....	0.35
Bonding.....	0.12
Total.....	<hr/> 0.47

In timbered sections where no supporting stulls are required, deduct 11 c. per ft. from the above costs, making a total of 36 c. per ft. In these figures, the cost of 2-0 Fig. 8 trolley wire is taken at 29 c. per lb., and 4-0 flexible bonds at \$1.26 each.

## The Ores in the Limestones at Bingham, Utah

BY RICHARD N. HUNT, LOS ANGELES, CALIF.

New York Meeting, February, 1924.

BINGHAM has produced 6 per cent. of this country's copper. In total production, it ranks fourth among the copper camps of North America, the order being Butte, Michigan, Bisbee, and Bingham. In its annual production, it held that same rank until 1919, when its production was exceeded by the combined production of the Globe-Miami district of Arizona.

Bingham has also been a lead camp of the first order. Utah ranks third among the lead-producing states, and its production comes largely from three camps which, in the order of their productivity, are: Bingham, Tintic, Park City.

Bingham's silver production is important, but it does not rank high as a silver producer. Utah owes its rank as first among the silver-producing states to Tintic, a camp 40 miles due south of Bingham. The United States Mineral Resources reports a total production from Bingham for the period 1865-1920 having a gross value of \$528,043,432.

### HISTORY OF THE BINGHAM DISTRICT

Bingham is on the eastern flank of the Oquirrh range 30 miles southwest of Salt Lake City, from which it can be reached in an hour by auto, or by the Denver & Rio Grande or the Bingham & Garfield railroads. The automobile route is a paved road across the floor of Great Salt Lake Valley, through farming country.

The Bingham & Garfield railway leaves the level of Great Salt Lake at the northern end of the Oquirrh range, and in 20 miles it climbs 2100 ft., and deposits the traveler upon a shelf cut in the side of Bingham Canyon below most of the mines, which are farther up Bingham Canyon and its tributary Carr Fork. Below lies the town, a narrow ribbon running for a couple of miles along the bottom of a canyon 2000 ft. deep—an almost impossible site for a community numbering, in prosperous times, 5000 to 7000 inhabitants drawn from all quarters of the globe. Up the canyon and down, and beneath the steep slopes nearby, and beneath the town itself, are the mining operations of over half a century.

During the past two decades one mine, the Utah Copper, has become so gigantic an operation as to dominate all other activity in the camp. It has become the greatest copper mine on the continent in production,

dividends disbursed, and reserves. Having produced 90,000,000 tons of copper ore, removed 54,500,000 yd. of capping, and paid \$123,000,000 in dividends, its reserves exceed 350,000,000 tons of 1.3 per cent. ore. Its success and well-merited fame have made "Utah Copper" and "Bingham" almost synonymous terms.

But before quantity production by Utah Copper began in 1907, other mines of the district had made Bingham an important producer of copper ore. These mines still yield considerable copper and lead-silver ores. They are "underground" mines, in contradistinction to the open-pit operations of Utah Copper. Their ores are derived almost exclusively from limestone horizons, which, with interruptions by faults and intrusive bodies, sweep across the entire district. The ores of Utah Copper and of two mines adjoining lie largely within the mass of a porphyritic intrusion, and will be referred to here as "porphyry" ores, while those from without the intrusive areas will be described collectively as "non-porphyry" or "limestone" ores. It is to the non-porphyry or limestone ores that attention is here primarily directed. The economic importance of the porphyry ores is much greater and their mineralogy and alterations are interesting; but in many respects the structural and metamorphic phenomena attending the occurrence of the limestone ores make them of far broader geologic interest. An excellent published description of the porphyry ores is that by J. J. Beeson.<sup>1</sup>

Bingham's history as a camp dates back to 1863. It seems that, unlike the more pastoral-minded Mormon settlers in the Salt Lake Valley, General Connor, commander of the third California Infantry stationed at Fort Douglas near Salt Lake City, took an active interest in the development of the mineral resources of the region; that he permitted his men to prospect the ranges bordering Great Salt Lake Valley; and that, in 1863, some of his soldiers together with a settler located the first mining claims in Utah on the outcrop of the Jordan Limestone in Galena Gulch, a tributary to Bingham Canyon.

The first shipment of ore is reported to have been made by Walker Brothers (Salt Lake City) to Baltimore in 1868. A railroad was built up to Bingham in 1873, four years after the completion of the Union and the Central Pacific Railroads.

Until 1897, Bingham's production consisted largely of silver, lead, and gold in that order of importance, reaching a total value in these metals of about \$39,000,000 and only \$1,075,000 in copper. Then followed the development and successful exploitation of copper ores in a property that, hitherto, had been a struggling gold prospect—the Highland Boy mine. This new development, together with the stimulus

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<sup>1</sup> Disseminated Copper Ores of Bingham Canyon, Utah. *Trans.* (1917) 54, 356.



to activity in other metals afforded by a drop in the price of silver, resulted in the discovery of other bodies of copper ore.

In 1904, the Utah Copper Co.'s production began, and in 1907, 1908, and 1909, respectively, the mills of the Utah Copper, the Boston Consolidated, and the Ohio Copper companies were completed and the era of quantity copper production in Bingham began.

A few years later, Utah Copper purchased the Boston Consolidated property. After an attempt to mine its low-grade ore by caving methods, the Ohio Copper suspended operations. But Utah Copper successfully expanded its operations until, today, its normal production is 35,000

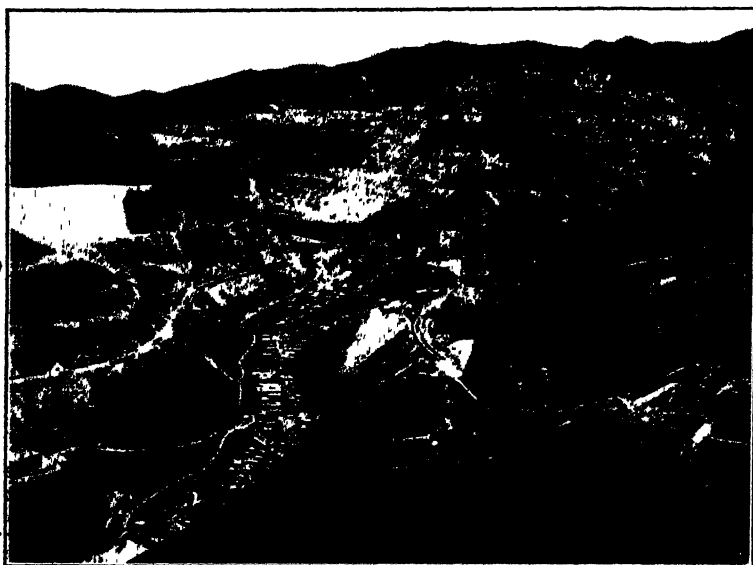


FIG. 1.—BINGHAM CANYON, UTAH COPPER HILL IN CENTER, TOWN OF BINGHAM BELOW, BINGHAM CANYON ON LEFT OF UTAH COPPER HILL, AND CARR FORK ON RIGHT.

to 40,000 tons of ore per day. During the past year, the Ohio Copper Co. has been recovering, by leaching in place, 600,000 to 700,000 lb. of copper per month from oxidation products (sulfates) formed in the fills and broken ore at and near the surface of its property.

#### BINGHAM MINING DISTRICT

The Bingham, or West Mountain, mining district covers 10 sq. mi. upon the eastern slopes and spurs of the Oquirrh Range. Deep dissection by Carr Fork and Bingham Canyon has developed a local relief of about 3500 ft. Heading near each other upon the south side of the district, and looping about Utah Copper Hill, these canyons converge to a union on the north in the town of Bingham. This central eminence, Utah

Copper Hill, comprising practically the Utah Copper property, is a huge three-sided pyramid rising 2000 ft. above the point of junction of the two canyons at its base. This pyramidal mountain, its sides cut into giant terraces and hidden beneath mammoth fills, all smoking and noisy with the industry of drills, steam shovels, waste and ore trains—confronts the visitor as he alights from the train, see Fig. 1. Contemplating that great pyramid, he may have to be reminded that upon all sides of it, beneath those slopes opposite it, are the “underground” mines that constituted the Bingham district as it was described by Boutwell,<sup>2</sup> in 1901, for the U. S. Geological Survey, mines which made it a camp of consequence while scrub oak and chaparral clothed the natural slopes of Utah Copper Hill. Today from these encircling mines come the non-porphry ores of Bingham. Chief among these mines are those of: The Utah Consolidated Mining Co., the Utah Apex Mining Co. the Utah Metal and Tunnel Co., the United States Mining, Refining and Smelting Co., the Montana-Bingham Consolidated Mining Co., and the Bingham Mines Co.

#### GEOLOGY, IN BRIEF

In the district are some 10,000 ft. of quartzite within which is a stratigraphic sequence of about 2000 ft. containing numerous lenses of limestone, some locally measuring 300 to 400 ft. in thickness. These beds have been folded into an open syncline plunging gently northwestward. In an axial position within this structure, and predominantly along the stratigraphic zone of these limestones, there has been injected an irregular outspreading mass of intrusive, “monzonitic” material. Within or along these limestones for 2000 to 3000 ft. away from and on either side of the main mass of the intrusive, but especially close to it and between its apophyses; in fissures and marginal positions within the intrusive itself; and to a minor extent along fissures in quartzite in the vicinity of mineralized limestone “beddings,” are the copper and lead ores of the camp.

#### *The Quartzite*

Quartzite is the dominant rock in the northern half of the Oquirrh range and in the Bingham district. It is a light-colored, pure, fine-grained quartzite, which with little variation forms a sequence of beds many thousands of feet thick. This, without subdivision, has been called the “Bingham Quartzite” and, on paleontological evidences, been assigned to the Upper Carboniferous. Throughout the northern end of the range, these quartzite beds have suffered moderate folding and faulting. As noted above, they have been warped into an open trough or synclinerium, whose axis strikes and plunges gently to the

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<sup>2</sup>Prof. Paper No. 38.

northwest, the average dip of the beds being about  $35^{\circ}$  to the north and west, but dips of  $90^{\circ}$  and even reverse dips are found.

The quartzite has an important, but negative, relation to the ores. In general, ore is not found in quartzite. Portions of the Utah Copper disseminated orebody and of its extensions into Ohio Copper ground are in fractured quartzite situated adjacent to the intrusive mass in which lies most of the Utah Copper orebody. Shattered quartzite along fault or sharp stratigraphic contacts with limestone, or adjacent to mineralized fissures, especially in the northern end of the camp, has locally contained ore. But altogether ores from such situations would constitute scarcely more than 2 or 3 per cent. of the camp's production. Quartzite is commonly regarded by the miner as unfavorable ground and is avoided in exploration work.

### *The Limestones*

In the camp proper and west and north of it are many beds of limestone ranging in thickness from a few inches to 400 ft. These vary

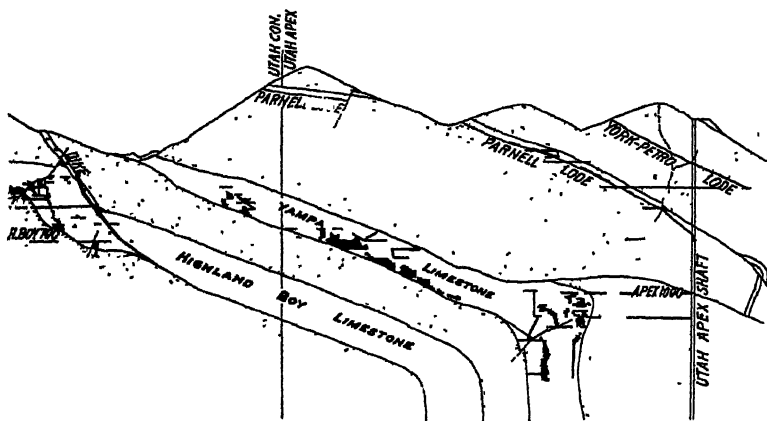


FIG. 2.—NORTH-SOUTH VERTICAL SECTION THROUGH THE HIGHLAND BOY, YAMPA, AND UTAH APEX MINES, SHOWING THE FOUR PRODUCTIVE LIMESTONE HORIZONS OF WEST SIDE OF DISTRICT.

rapidly and greatly in thickness from place to place, being lenticular in form and extent. Representing only temporary, and more or less rhythmical variations in the dominant process of sand deposition, they are truly integral parts of the thick Bingham quartzite formation. Within the general region of the Oquirrh Range, these limestones are more or less local. But within the productive limits of the district, a few are sufficiently continuous to be regarded as definite horizons. Furthermore, they have come to have so great an economic value and significance that they have been named and recognized as members of a definite stratigraphic succession. There are three principal horizons in this

succession, which, from the lowest upward and in the order of average thickness, mass, extent, and economic value, are:

The Jordan or Highland Boy Limestone

The Commercial or Yampa Limestone

The Parnell-Petro or Mayflower-Fortuna-Winnebago Series



FIG. 3.—SOUTHWEST AND CENTRAL PARTS OF DISTRICT, SHOWING BLOTTING OUT OF LIMESTONES BY PORPHYRY INTRUSIONS, AND RELATIONS OF HIGHLAND BOY AND YAMPA LIMESTONES TO JORDAN AND COMMERCIAL, RESPECTIVELY, ON OPPOSITE SIDES OF UTAH COPPER HILL; COORDINATE INTERVAL, 500 FT.

The first two are massive strata commonly more than 200 ft. thick. The third consists of a series of thin limestones, each a few feet thick,

alternating with relatively thicker quartzite beds. These three horizons are separated from one another by 300 to 800 ft. of quartzite. Their relative thickness and position are shown in the vertical section of Fig. 2.

Entering the district upon the west, these limestones sweep eastward through the properties of the Utah Metal and Tunnel Co., the Utah Consolidated Mining Co., the Utah Apex Mining Co., and the Utah Copper Hill, the Utah Copper, and United States; then, swinging gradually to the northeast and north, they pass through the properties of the Bingham mines, the Montana-Bingham, and other companies, see Fig. 3. Throughout, their course conforms with the synclinal structure of the camp but with interruptions by monzonite intrusives and, to a lesser extent, by faults. Occurring here and there between these principal beds of limestone and in the quartzite overlying and underlying them as a group are other limestones. These are limited in extent and, save where one may have yielded considerable ore, have received no names or consideration.\*

These limestone horizons have greatly influenced the distribution of the non-porphyry ores. They are one of the two dominating factors controlling the distribution of Bingham ores; their influence seems to have been essentially physico-chemical in its nature. In their extensive replacement by ore minerals, they are in the strongest possible contrast to the more abundant and apparently resistant and refractory quartzite with which they are intercalated. For hundreds of feet, even as much as a thousand in places, sometimes from foot wall to hanging wall, their whole mass, like a sponge, became permeated with ore minerals and alteration products. Although these limestone horizons constitute less than one-fifth, by volume, of the productive ground of the district, they have produced upwards of 95 per cent. of the non-porphyry ores of the camp.

### *. The Igneous Rocks*

The igneous rocks of the camp are intrusives. With minor exceptions, they are acid, being generally described as monzonite porphyry.

They cover fully one quarter of the productive area. About half the bulk of Utah Copper Hill consists of porphyry, which is part of a much more extensive and highly irregular mass, the major dimensions of which approach parallelism with the regional strike and dip of the sediments. From this sprawling central mass, in a small part of which occur the ores of Utah Copper, many branches reach out into the sediments, especially to the west and to the northeast, following the general course of the beds and rapidly decreasing in mass as the distance from the central porphyry areas increases. As these apophyses become smaller and extend farther from the parent mass, they tend toward strict paral-

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\*Some distance stratigraphically beneath the Jordan limestone in the United States mine are two beds of limestone which have yielded very considerable ton-nages of lead ore.

lelism with the bedding. At distances from the center of the district, the intrusive masses are almost without exception sills.

The porphyry consists of varying proportions of orthoclase and plagioclase feldspar, biotite, hornblende, augite, quartz, and their metamorphic successors. Quartz is abundant in places, particularly in so-called "light" or "siliceous" phases of the porphyry, where much of it, however, is not a primary constituent. But to the eye quartz is often not an easily observed constituent, the rock appearing to consist of feldspar and the ferromagnesian minerals. The more prominent phenocryst minerals are feldspars. But in many phases, especially in the finer grained ones, the phenocrysts are biotite. The texture varies from that of a fine felty mass, gray when fresh, gray-green to rusty brown when weathered, to a grain so coarse that the feldspars may average  $\frac{1}{2}$  in. and attain 1 or 2 in. in length.

A few occurrences of other igneous types have been found. In the Utah Apex and Utah Metals mines are thin sills of dark basaltic type. At a point in the Utah Metals mine, material sampled and thought to be altered quartzite proved to be rhyolite. A small rhyolite dike appears also upon the 1300-ft. level of the Highland Boy mine.

#### *Age of the Porphyry*

Whether the intrusives are all of one age is not known. In a broad way, they probably are. In two widely separated areas and near the contacts of large porphyry masses are numerous, angular, and frequently sharp-edged inclusions of slightly differing textures and compositions. Quartzite fragments are also present in these contact breccias; Boutwell describes hornblende diorite fragments, a rock not found within the district. But these seem phenomena to be explained by the conditions and mechanics of intrusion; and are not necessarily evidence of two or more generations of porphyry distinctly separated in time.

I believe that nowhere has a clear crossing or intersection of one intrusive by another been found. This negative fact, together with the general uniformity in composition and the structural continuity and unity of the porphyry areas—they are all connected and in general emerge from two large central masses—suggests one general period of intrusion.

#### *Time of Intrusion*

There is no means of fixing the time of the intrusion. We know only that it is post-Carboniferous, and probably earlier than andesite flows and agglomerates found at the edge of the valley and foot of the range, which are so late as to occupy depressions in the present topography. The time relations of intrusion to regional folding are also indeterminate. The fact that the general attitude of the sedimentary rocks throughout the district, and even in small areas nearly surrounded by porphyry, is in strict accord with the synclinal structure imposed on the whole area

may indicate that intrusion was subsequent to the regional folding. But this is a difficult matter on which to generalize. It is somewhat complicated by the presence of local folds of "rolls," which in their axial relations are not always in agreement with those of the master synclinal structure. These are terrace-like irregularities that, on their plunge, sometimes break into faults of moderate displacement. Though they may cause displacements of a few hundred feet, they are local features that play out in directions parallel to themselves and normal to the bedding. They are essentially features of the stratigraphic zone embracing the thicker limestone members and seldom affect the quartzite beds higher in the series. In an interesting fashion, they disclose the great difference in competency between the limestone and the quartzite, in

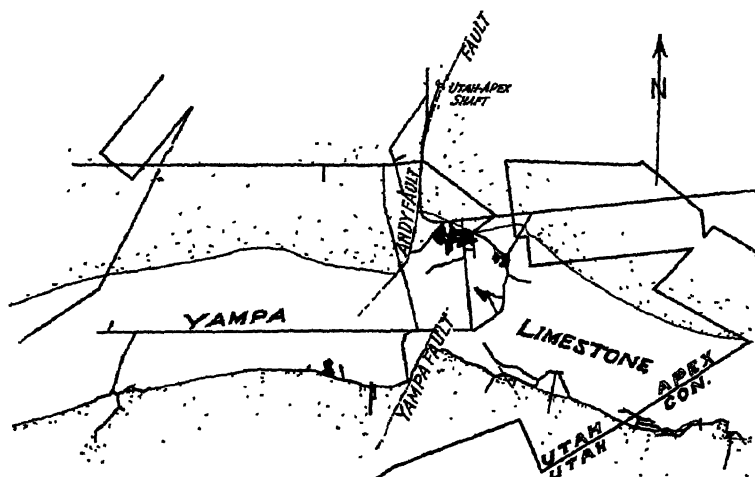


FIG. 4.—UTAH APEX AND HIGHLAND BOY WORKINGS ON PLANE OF UTAH APEX 1000-FT. LEVEL, SHOWING A FAULT FOLD IN YAMPA LIMESTONE, QUARTZITE BOTH NORTH AND SOUTH, LIMESTONE BEING FAULTED AND LIMESTONE WARPED INTO A TERRACE-LIKE FOLD.

the same structure the limestone yielding by folding and the quartzite by breaking, see Fig. 4. These fault folds, so to speak, are obviously related both in causal stress and in time to late cross faults with which they are structurally inseparable. Therefore, because in such folds dikes and sills are sometimes sheared and displaced, they do not invalidate the suggestion that intrusion occurred subsequent to the general folding.

#### *Relations of Intrusives to Ores*

The intrusive masses have a most direct and controlling relation to the ores of the camp, both in a broad areal way and in the detailed occurrence of many individual orebodies. The porphyry masses antedate the ores but so definite are the relations of geographic distribution and of certain mineralogical zonal relations of the ores to the areas of the por-

phyry, that there can be no question of a genetic relation between them. The ores may be definitely ascribed to the agencies and sources related to and responsible for the porphyry itself; and, speaking of the region broadly, as incidents in that intrusive process they are localized in the vicinity of the porphyry. Furthermore, distance from the intrusive center is a factor determining not only the character of the alterations in the country rock but also the character of the ore.

### *Faults*

Although numerous in the district as a whole, faults are not major structural features. Their displacements are usually less than 200 ft., they are of varying ages, some being pre-mineral, some post-mineral and some both. They may be conveniently divided into two general classes, "cross faults" and "strike" or bedding faults.

Cross faults usually strike north or northeast and dip steeper than 45°; a few, notably a large one, the Occidental, strike northwest. Some displace porphyry masses; others, such as the Ball fault in the Highland Boy mine, have been followed by dikes. Many cut through and displace intrusions and are post-porphyry as regards, at least, the last movement along them. In general, there have been repeated movements along cross faults.

Strike or bedding faults strike with the sedimentary formations, and usually coincide with them also in dip. There are, affecting the Highland Boy limestone in the upper part of the Highland Boy mine, some faults, however, that strike with the beds, but dip more steeply. Bedding faults are common along foot-wall stratigraphic contacts of limestones. The term fault is used loosely, here, to include fissures containing only gouge material and lacking other evidence of actual displacement.

Porphyry masses are rarely displaced along bedding faults, but frequently sills of porphyry lie in them, as in the case of those along the foot wall of the Yampa Limestone in the Highland Boy mine, and the Stoddard-Malloy bedding in the Utah Metals mine. It might be noted that if the adjustments represented by bedding faults are incident to the folding, as has been suggested and as some meager evidence relating to drag cleavage indicates, the presence of porphyry sills in bedding faults (sometimes sheared, sometimes not) suggests that folding was prior to the intrusion of the porphyry. In general, bedding faults are probably pre-porphyry and pre-mineral in age.

### *Relations Faults to Ores*

Ordinarily, the obvious relation of the cross faults to ores is that of post-mineral faults terminating and offsetting them, and in such cases of terminated orebodies, the displaced portions are usually only short distances away. If the orebody is large, 100 ft. or so in extent, measuring parallel to the plane of the fault, it is ordinarily not completely severed,



its segments overlapping. But occasionally cross faults are mineralized or orebodies within the thicker limestones are so arranged with reference to them as to suggest that the fault as a relatively more pervious zone influenced the course of the mineralizing agents.

Bedding and strike faults, however, are the site of many and extensive bodies of ore, which may lie vein-like, in or along their gages or may have extensions upward or downward into the mass of the limestone.

In the upper part of the sedimentaries and more northern portions of the camp, namely, in Cottonwood, Dixon, and Markham gulches, thin sheets of mineralization locally containing small bodies of ore (usually lead ore) occur frequently along sharp stratigraphic contacts between thin limestone lenses and quartzite. Such are the deposits prospected and to a small extent mined along the I. X. L., McCann, Julian and Butler beddings in the Bingham and Eastern and Bingham Coalition properties.

### *The Ores*

The first impression is that of a general bunching of the ores near and upon both sides of the central porphyry mass of Utah Copper Hill. In this respect one is reminded of a similar clustering of the orebodies in the limestones of Bisbee about the nuclear core of mineralized porphyry in Sacramento Hill. However, in Bisbee a fault, which brings up siliceous, pre-Cambrian schists upon the one side of Sacramento Hill, confines the productive area to the 180° sector of limestone upon the other side of the fault and hill. In Bingham, the ores come nearer to occupying the 360° of radial sweep about Utah Copper Hill. But, as in Bisbee, the ores are in limestone, which really limits them to two large segments upon opposite sides of Utah Copper Hill with relatively unproductive quartzite and porphyry segments in between on the northwest and southwest sides, respectively.

The ores are within an area of relatively small radius about Utah Copper Hill. Proceeding in any direction  $2\frac{1}{2}$  miles, one passes beyond all known ore occurrences. The greatest distances are west and northeast along the strike of the limestones, while the lesser are north and south normal to their strike. But a circle less than a mile in diameter with its center on the top of Utah Copper Hill would encompass the region from which has come probably 80 per cent. of the camp's non-porphyry ore production and 95 per cent., or more, of the camp's total production. Such a circle includes the most productive portions of the Highland Boy, the Utah Apex, the Utah Metals, the old Yampa, the old Boston Consolidated or Sulphide, and the New England mines upon the west side of Utah Copper Hill, and the old Jordan, Commercial, Niagara, and Telegraph mines upon the east, the last four comprising and being known collectively as the U. S. Mine. Though ores are found in considerable quantity beyond this circle, especially to the northwest in properties

now worked by the Bingham Mines Co., the great tonnages of the camp have been mined from within this limited area. The massing of the ores about the center of intrusive activity, and the tremendous increase in productivity as this center is approached, is assuredly significant of the potent influence of the porphyry.

### *Relations to Type of Rock*

Ores are found in all formational types: quartzite, porphyry, and limestone. Occurrences in the dominant and most widespread rock, quartzite, however, are rare, relatively small, and, for the most part, sporadic deposits that are usually near, if not actually, selvage portions of larger bodies of ore in porphyry or limestone. The disseminated ores of Utah Copper are the single example of profitably mined ores in the mass of the porphyry. And they are not ores in the same sense as the deposits worked in the underground mines. They are ores because of tonnage and extent, and would have no economic value if scattered through a considerable volume of ground in unit masses of a few thousand to a hundred thousand tons each. Small fissures in porphyry, such as those worked in the old New England mine, have yielded small tonnages, in the instance mentioned, of zincy-lead ore. Occasionally, a fissure in a contact situation between porphyry and sedimentary material may yield high-grade ores, even where locally both walls are porphyry. Such is true of certain occurrences in the old Utah Metals and Bingham-New Haven mines, now owned by the Utah Metal and Tunnel Co. Low-grade ores in quartzite and porphyry were for a time worked by the Ohio Copper Mining Co. and have recently proved to be amenable to an interesting method of leaching *in situ*. But taken altogether, these and other non-limestone ore occurrences, except those of Utah Copper, are unimportant in comparison with the limestone ores.

### *Non-porphyry Ore Confined to Limestones*

Practically, the entire production of non-porphyry ores is derived from the three principal limestone horizons already described. With remarkable precision, these horizons include within their sweep across the district those properties that have met with some success, and exclude the hopeless failures. Their extent determines and limits the region of productivity and of favorable prospecting ground. Their direction of dip is the direction of development and downward growth of the mines located upon them. Over half a century of continuous development and hundreds of miles of mine workings have established these relations as a principal fundamental to the conduct of explorations.

In general, the relative productivity of these horizons happens to be proportional to average thickness. The following table includes totals up to 1919 for a definite area in the western half of the camp.

Within the area of these calculations are the Highland Boy, the old Yampa, the Utah Apex mines, and parts of adjacent properties.

	Tons
Highland Boy Limestone.....	4,224,820
Yampa (Parvenu) Limestone.....	2,367,400
Parnell—Petro Series.....	748,250

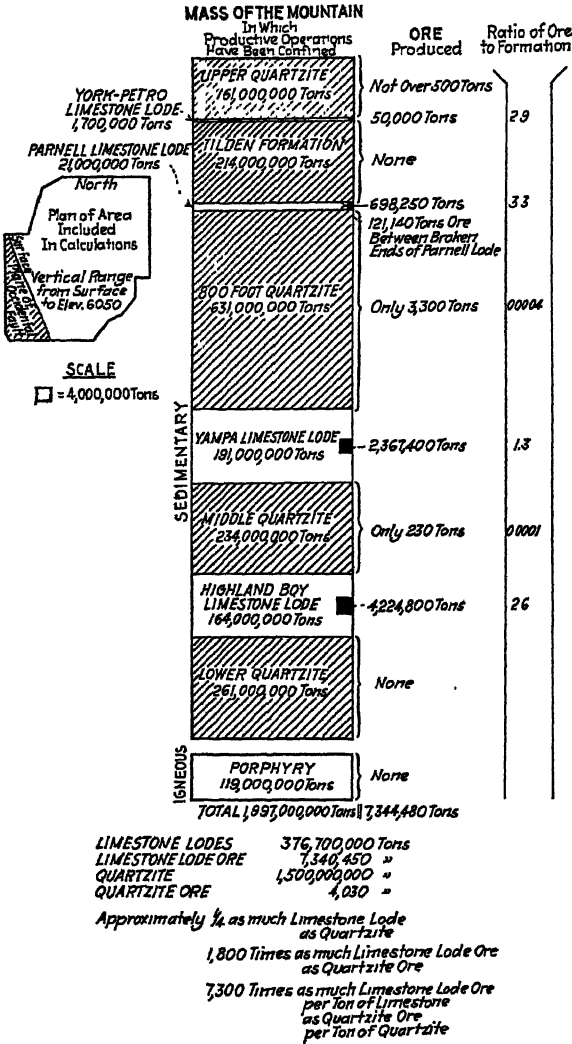


FIG. 5.—GRAPHIC ANALYSIS, SHOWING RELATION BETWEEN FORMATIONS AND ORES IN TERRITORY OF UTAH CONSOLIDATED AND UTAH APEX MINING CO. (PREPARED BY PERRY G. HARRISON AND A. E. ROBINSON.)

These same relations are shown in Fig. 5, which in addition contains mass ratios of ore to limestone and limestone to the quartzite and por-

phyry present in the western portion of the camp. As much as 2.6 per cent. of the total mass of the Highland Boy limestone within the area of the calculations was actually removed as ore.

### *Distribution Within the Limestones*

The ores are most generously and widely distributed throughout the thickness of these limestones and for great distances measured outward along their strike from the central porphyry area, and from the surface to the greatest depth yet attained by workings, 2500 ft. vertically or 5000 ft. on the dip of the limestones. Structural features, such as bedding, fissures, and dikes, have in some cases determined the local distribution of ores. In many other instances, these features seem to have had no influence whatsoever. Ores are abundant in both highly altered limestone and in limestone practically unaltered; but are most abundant in the metamorphosed areas. The ores themselves vary in character with the degree of metamorphism. This relation between types of ore and distinct conditions of alteration is one of the most instructive and fascinating aspects of Bingham geology, and will be more fully considered later.

### *Oxide Zone Poorly Developed: Ores Essentially Primary*

Though a distinct oxide and a secondarily enriched zone are present in the limestone areas, in comparison with many camps of the southwest and Mexico, they are not highly developed features and are, locally, so poorly developed as scarcely to be present at all. In the outcrops of the Jordan and Commercial limestones are minable bodies of copper carbonates and oxides. Similarly, the outcrops of the Yampa and Highland Boy limestones are stained with carbonates and much iron oxide; but in the latter, less than 50 ft. below the surface, occur only slightly oxidized, pyritic ores. In many of the Highland Boy stopes nearest the surface (100-300 ft.) were the highest grade copper ores of the mine; and only in the upper levels of the mine did chalcocite appear conspicuously and from a quantitatively important ore mineral. In the upper workings of the old Boston Consolidated and Jordan mines, in the Jordan and Commercial limestones, were some oxidized copper ores. In fact, in the higher portions of these properties, I believe, is the best development of oxide ores in the camp.

But the great bulk of the limestone ores have been 2 to 3 per cent. sulfide ores, whose copper is largely in chalcopyrite, and whose low gold and silver content is intimately associated with both the copper and the iron sulfides, pyrite being by far the most abundant and conspicuous ore mineral.

Lead ores near the surface are usually carbonates, but at a comparatively few feet down galena appears and becomes the principal lead min-

eral. The many small lead veins of the old New England mine illustrate these relations. From many of the stopes upon the so-called Stoddard, Malloy, and Zelnora beddings in the western and higher portion of the Utah Metals mine came lead-carbonate ores with minor amounts of residual galena. A few stopes in the Boston Consolidated yielded lead-carbonate ores, but most of the lead-silver ores of the district are sulfide ores. With the galena ordinarily occurs some sphalerite; sometimes the percentage of zinc present exceeds that of lead.

With regard to the limestones, the distribution of what within this camp might be called areas of abundant oxide ores and the general absence of a well-developed, deep oxide zone here, where a desert climate, relief and presumably many of the same factors are present that in so many camps of the Southwest and Mexico have produced deep oxide-enrichment zones, is an interesting feature. It might be suggested that it is a condition to be explained in part by the recent topographic history of Bingham.

Bingham is in the Lake Bonneville basin, a region of peculiar and recent topographic and water-level change. It is a region of great blocks that, alternately, are: upstanding, deeply dissected ranges, and wide, deeply filled valleys. The changes in elevation, measurable in hundreds of feet, and even faulting of Lake Bonneville terraces, show it to be a region of recent and probably present ground movements deep-seated and regional in character.

Bingham Canyon, Carr Fork, and their tributary gulches are deep, V-shaped trenches, the lower slopes of which range from  $30^{\circ}$  to  $40^{\circ}$ . Their bottoms are clean-swept, usually exposing bedrock. They are young down-cutting channels that, in times of freshet, sweep tremendous volumes of material out into Jordan valley. But here and there, sometimes as much as 400 ft. above the bottom of the canyon, are remnants of conglomerate beds representing some past topographic period during which the present canyons were filled to a depth well above the elevation of most of the present orebodies. There has recently been a renewal of erosion and a rapid cleaning out and deepening of drainage lines. The principal areas of carbonate ores are situated at high elevations under divides in the uppermost reaches of these canyons and their tributaries. Whereas, lower down and beneath their main channels sulfide ores, without evidence of other than primary minerals, come to within a few feet of outcropping. The suggestion seems warranted that whatever oxide zone may have formerly been developed over the central and most productive portion of the limestones has now been removed by erosion operating, in this case, more rapidly than the agencies of oxidation and enrichment.

It is interesting to note, in regard to oxidation and enrichment, that the case seems somewhat different in the porphyry ores. Any vertical section through the Utah Copper orebody shows an oxidized superficial

zone, 50 to 150 ft. deep, carrying 0 to 0.8 per cent. copper. Below this zone, in both the Utah Copper and the Ohio Copper properties, a considerable proportion of the minerals—and a most important proportion, making in these low-grade ores the difference between ore and waste—consists of specks and coatings of chalcocite, which is regarded as secondary to an earlier deposition of pyrite, chalcopyrite, bornite, and possibly, chalcocite. The enrichment of these porphyry ores, though a process of great economic importance, from the point of view of the amount of material transported in this case as compared with cases of thorough secondary action elsewhere, is probably a process of small effectiveness. But under any circumstances, no doubt, the acid porphyry facilitates the migration of values to a greater extent than do the limestones. In fact, the deeper development of the characteristics of oxide and secondarily enriched sulfide zones in the porphyry and their absence or paucity in the lower limestone areas may be a measure of the rapidity of erosion—erosion being, so to speak, a lap ahead of secondary concentration in the lower limestone areas and one behind in the porphyry areas.

### *The Copper Ores*

In the detailed discussion of ores, the writer has the western half of the camp, with which he is somewhat better acquainted, more in mind than the eastern; but the differences between the eastern and western parts of the district are matters of degree more than of kind.

The copper ores, apart from a few occurrences, seldom run much above 3 per cent.; and the production of one of the most successful of the mines, the Highland Boy, has for years averaged about 2.5 per cent. copper. The Highland Boy ores usually carry a little over a dollar in gold and silver, and at periods in the history of this mine have received a premium from the smelter for the excess iron present as pyrite. This mine, which has paid about \$14,000,000 in dividends, is remarkable for the low grade of its ore notwithstanding the fact that its stopes must be methodically timbered, usually square-setted, are systematically filled, and reach to a considerable depth. Pumping has been necessary for many years; and for years the mine was situated  $1\frac{1}{2}$  mile up a steep canyon from the nearest railroad spur. Until 1921, the mine was without a mill, but it has enjoyed the benefit of cheap transportation to the International smelter at Tooele, to which its ores are conveyed by a 4-mile aerial tramway at a cost of 30 c. per ton.

The Yampa, Boston Consolidated, and other properties have also produced large tonnages of low-grade pyritic copper ores. The Utah Apex mined some copper from its Parnell York-Petro beddings in its upper and older workings. From the properties of the United States Co. and others on the east side of the camp have come large tonnages of

copper ores; in some of these properties remain partly developed areas of low-grade copper ore and mineralization.

As copper ores go, the Bingham ores are of exceptionally low grade. In the great bulk of them, copper minerals are rarely seen without a lens. They are lost in a gangue consisting largely of pyrite, which sometimes constitutes over 75 per cent. of the mass of the ore. The gold and silver values are intimately associated with the sulfides, both copper and iron. But operations at the new Utah Consolidated mill, which treats daily 1000 to 1100 tons of ore coming from both the Yampa and Highland Boy limestones, show clearly that the greater part of the gold and silver occurs either in separate mineral form or in intimate association with the copper. At the mill, through differential flotation 85 per cent. of the pyrite is dropped, yet 65 per cent. of the gold and silver is recovered.

#### *Copper Ores Largely Metasomatic Replacements in Altered Limestone*

These copper ores occur typically in large irregular masses that are replacements of the limestone. Frequently every textural and structural feature of the limestone is preserved perfectly in the massive sulfides. Often the strike and the dip of the bedding may be as accurately observed in the middle of a massive orebody as in the laterals adjacent in unreplaced limestone. The greater dimensions of these orebodies, which often reach into hundreds of feet, usually lie in the plane of the bedding. Faults and dikes may determine their form in detail, but such influence usually does not amount to that of an exclusive or sole localizing agent. These large replacement bodies are characteristic of the highly altered portions of limestone within 1500–2000 ft. of the central porphyry area. In their vicinity, the limestone may be so completely metamorphosed as to contain no lime carbonate at all, and to be composed of solid masses of high-temperature minerals, notably, garnet, wollastonite, and diopside. Tremolite, asbestos, and specularite are also common in these highly altered areas. As the limits of high-temperature effects are approached within these limestones, which in effect means as one proceeds westward or eastward along their strike away from the central porphyry area, first come lime silicate and crystalline carbonate phases; there are all transitional stages between pure silicate rocks and fairly pure marble. Proceeding farther outward along the beds, these white marbleized and silicated facies become more streaked with gray-to-black bands of unaltered limestone. The normal, unaltered limestone in Bingham is dark gray to black and stands in such strong contrast to the snow-white and delicate creamy tints of the altered material that the terms "white" and "black" limestone are common among miners and engineers and are the first descriptive terms used in describing conditions existing at any given prospecting face. Because the greater part of the ores, almost all of the

copper ores, are from out the "white" limestone, the two terms come near having the significance of "good" and "bad."

A projection, Fig. 6, to a horizontal plane of the workings and conditions within the Highland Boy limestone (which is a bed 300 ft. thick

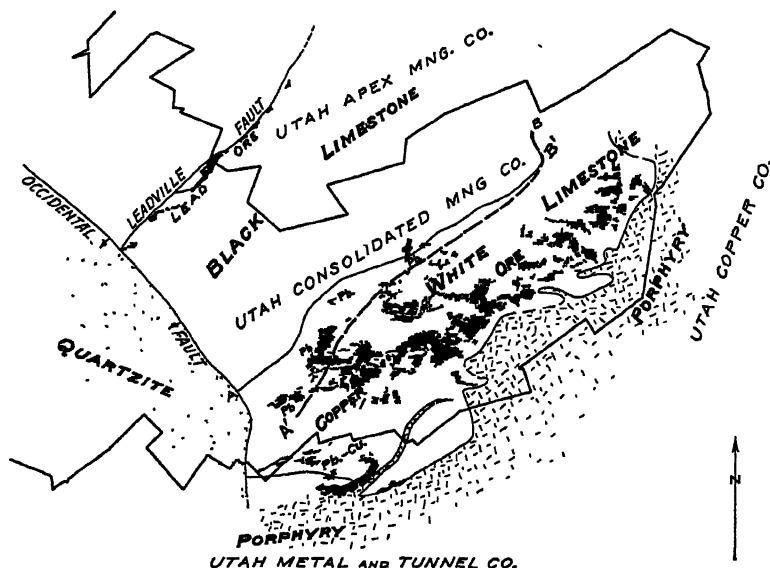


FIG. 6.—COPPER AND LEAD STOPS IN HIGHLAND BOY LIMESTONES, SHOWING THEIR DISTRIBUTION RELATIVE TO ONE ANOTHER, THE PORPHYRY, AND AREAS OF WHITE (ALTERED) AND BLACK (UNALTERED) LIMESTONE.

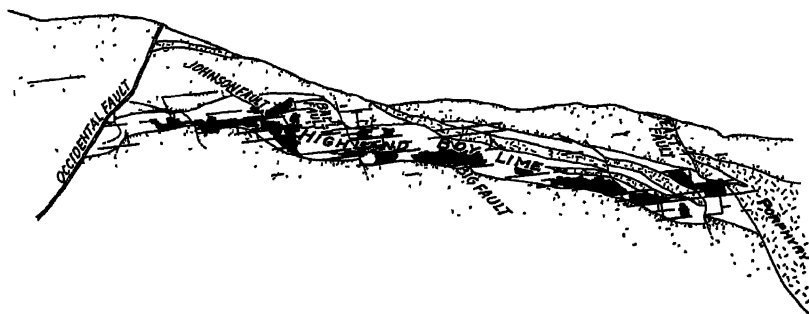


FIG. 7.—VERTICAL SECTION NORTHEAST THROUGH COPPER REPLACEMENT OREBODIES IN HIGHLAND BOY LIMESTONE, SHOWING THEIR CONFINEMENT TO THAT FORMATION.

dipping northerly throughout most of the area of this map at an angle of about 35°) shows the confinement of these large replacement orebodies to the "white" or altered limestone area. It also shows well the parallelism of this highly productive belt of "white" lime to the main mass of porphyry on the southeast. Within this area are several dikes that



extend far out between these orebodies and overlies many of them, which could not be more than partly indicated without too greatly complicating the map. It should be noticed that the lead stopes (marked Pb) within this area are in the outer margin of this belt of altered limestone or out in the large area of the "black" or unaltered limestone. Fig. 7 is a vertical section through the copper stopes shown in Fig. 6.

### *Vein-like Copper Orebodies: Beddings*

Besides these large irregular deposits, within the mass of these limestones are vein-like bodies in or along fissures, bedding planes, and intrusive contacts. These are often massive sulfide bodies, consisting largely of pyrite and of very little quartz or other gangue materials, and with copper largely in chalcopyrite, and a little gold and silver. These are not large, ordinarily, except in the case of bodies along the foot-wall bedding planes of some of the limestones, notably, the so-called Yampa "contact" or "foot-wall" orebodies, and those of the Parnell limestone in the Utah Apex mine, which are extensive shoot-like deposits of both copper and lead ores. These occurrences are known locally as bedding fissures, or "beddings," a good descriptive term.

In part, these are replacement ores. There is often scattering mineralization far out into the walls beyond the limit of minable ore, especially in the overlying limestone. These are sometimes extensions into the mass of the country rock, which themselves, at least, are replacements of pre-existing materials. In the main, these beddings represent the replacement of pre-existing fissure or fault filling, gouge, and breccias.

But some of the heavier sulfide material, especially that developed during recent years, at depths of 2000 ft. and greater, in the Highland Boy, may be injections similar in origin and their manner of entry to thin porphyritic intrusives, which themselves often occupy similar sites, *i. e.*, along bedding planes. Local sharp contacts between solid sulfide masses and slightly or unmineralized materials and the occasional fragments of quartzite and porphyry to be found embedded within and unreplaced by sulfides, seem to suggest such relations. Local bandings may also represent flow structure; but always such evidence is ambiguous as it may equally well represent the perfect metasomatic replacement of a previously banded gouge or other material. This is a theoretical subject requiring most careful study; I am not prepared to discuss it here and wish only to suggest an origin that has often occurred to me, and which I am now the more emboldened to suggest because of the advancement by Spurr, in his recent book "The Ore Magmas," of the conception of "vein dikes," a term that I believe will find a permanent place in the geologist's tool kit, whatever disagreement there may be to some specific applications of it by Spurr.

*The Lead Ores*

Lead ores, consisting of galena, pyrite, and widely varying proportions of sphalerite, minor quantities of copper and other metals, notably silver, often in the ratio of an ounce of silver to 2 per cent. of lead, have been found in all types of rock and in all parts of the productive area. Many fissures in porphyry in the New England and Last Chance mines carried 6 to 18 in. of banded lead-zinc and zinc-lead ores. Bedding fissures, especially along quartzite-limestone stratigraphic contacts, on both the east and the west side of the camp, have produced much lead ore. Stopes

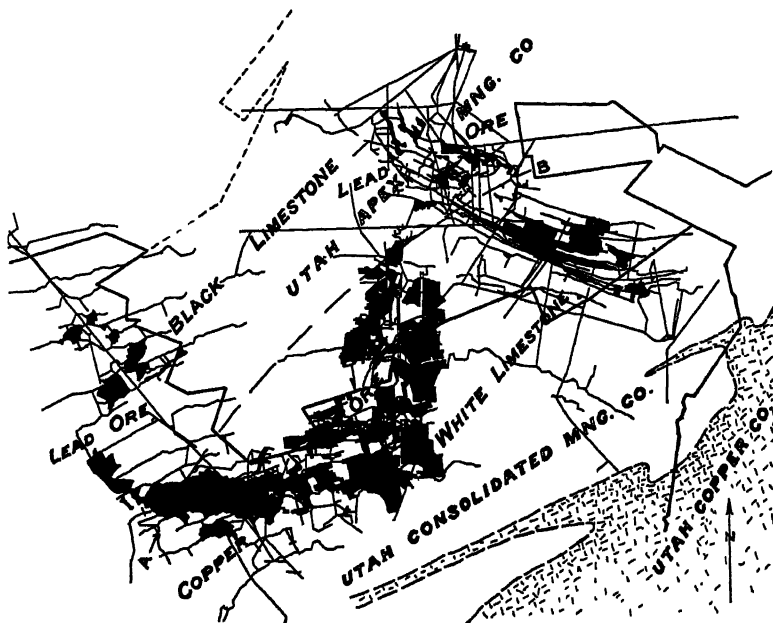


FIG. 8.—PRINCIPAL WORKINGS AND STOPES IN YAMPA LIMESTONE PROJECTED TO A HORIZONTAL PLANE, SHOWING DISTRIBUTION OF LEAD AND COPPER ORES IN THAT LIMESTONE TO MAIN MASS OF PORPHYRY, AND TO AREAS OF WHITE (ALTERED) AND BLACK (UNALTERED) LIMESTONE.

within the mass of the Parnell and Yampa limestones within the Utah Apex mine have yielded lead ores, which have constituted the bulk of that mine's production.

In the old Yampa mine, and western portions of the Highland Boy mine (in the Highland Boy Limestone), are large square-set stopes that yielded millions of dollars worth of lead-silver ores. The Utah Metals and the old Boston Consolidated mine in Utah Copper Hill produced a large tonnage of lead ore, as have also many of the properties on the east side of the district, which are now consolidated and under the management of the United States Mining and the Bingham Mines companies.

The United States mines have for years been among the great lead producers of the state.

The general form and situation of the lead orebodies is not greatly different from those of copper; but there is a marked difference in their geographic distribution, as was pointed out with reference to Fig. 6. There, the line *AB* marks the change from white to black limestone and the line *A'B'* separates two areas within the limestone in one of which occurs 95 per cent. of the copper ores thus far mined and in the other nearly as high a percentage of the lead ores. The general parallelism of these lines to that of the porphyry contact is striking.

Similarly, in the Yampa limestone, which lies some 300–400 ft. directly above the Highland Boy (see Fig. 2) is an areal segregation of lead and copper ores. In Fig. 8, which shows the stopes and workings of the Utah Apex and Highland Boy mines within the Yampa limestone, the line *AB* definitely separates an area of predominantly lead ore from one of copper. Here, also, this line is approximately that between the areas of white and black limestone and is rudely parallel with the contact of the main porphyry mass. It should be also noted that the line of change from white to black limestone is nowhere far distant from most of the lead orebodies on whichever side of it they may lie.

There is here, I believe, a relation, of broad significance and one throwing unusual light on the processes of ore deposition.

### *Zonal Relations of Copper and Lead Ores*

In the distribution of the lead ores with reference both to those of copper and to the porphyry areas, there is a striking and almost graphic situation. In the center of the productive area is this sprawling intrusive reaching out with long tapering fingers, 1000 to 2000 ft. through these limestones and quartzites. In the limestones, between these fingers, and clustering close about the larger and parent mass of porphyry are the large copper orebodies, which become less numerous and less extensive the farther one proceeds radially from this central mass of porphyry. But as one approaches a fairly definite zone 1500 to 2000 ft. from the porphyry, measuring horizontally along the strike of the limestones (or a somewhat greater distance in any inclined or vertical direction), small bodies of lead ore begin to appear, first, intermingled with copper ore (the same stope producing both copper and lead ore) and, then, lead ore free of all but mere traces of copper. Such a progressive change horizontally along the strike of the beds and normal to the porphyry contact is not a matter of a single development on a single level. On level after level, the old Nos. 4, 5, 6, 7 tunnel levels, and on the 9, 13, 14, 16, and 18 levels of the Highland Boy, the same succession of changes can be traced. These are developments within the Highland Boy limestone. The same change, proceeding east to west, occurs in the ores of the overlying limestone, the Yampa,

mined in both the Utah Apex and portions of the Highland Boy mines; and again in the still higher horizon, the Parnell bedding, mined in the upper workings of the Utah Apex, see Fig. 2.

### *Leadville Orebodies*

Out some distance, but within the area of black limestone and shown on Fig. 6, are a group of orebodies known as the "Leadville country." They are a northeast-southwest chain of orebodies about 2500 ft. long extending from the elevation of the Highland Boy 1000-ft. level down to the 1800-ft. level. They lie within the Highland Boy limestone, along a peculiarly deformed zone, in which the quartzites overlying and underlying the Highland Boy and Yampa limestone formations respectively have been faulted; but the limestones have accomplished the same adjustment in part by folding and with little breaking. As far as the limestone is concerned, the structure may be aptly described as a "fault fold."

This group of lead ores is not so far from either porphyry or white limestone as it appears to be on Fig. 6; on the lower levels, white limestone and some porphyry dikes appear beneath the lower or northeastern end of these orebodies. As these lead ores were followed downward into this lower area of altered limestone, some copper ores were found, which persisted in varying proportions to below the 1600-ft. level.

### *East Side of the District*

Similarly, on the eastern side of the camp, the great copper replacement orebodies are in the mass of limestones abutting and cut by offshoots of the porphyry of Utah Copper Hill; lead ores occur here also. Farther to the northeast and north, outward along the course of these limestones, in the Brooklin, Yosemite, and other of the Bingham mines group of properties, both lead and copper ores have been mined, but the outermost bodies on the borders of the productive area are lead ores.

Of course, it must be understood that in speaking of two types of ores, copper and lead, there is a commercial element in the distinction which sometimes is more important than the mineralogical differences present. Occasionally ores will carry considerable of both lead and copper; the rating of the ore as the one type or the other may then be determined by the treatment accorded it at the smelter, and it is classed as the one or the other according to whichever rating brings the best return under existing smelter contracts. But usually the segregation of the lead and copper is such as to produce ores distinctively of one type or the other. Sometimes, however, the intermingling within one stope of two even distinct types is such that they are difficultly separated in mining. The lead ore may wedge in along the foot wall or hanging wall of the copper ore or it may form interpenetrating bands through it, along the bedding, or, perhaps, a fissure. But even here, where separation in mining may

be difficult, the segregation of the two types is usually distinct, so that one may take good-sized specimens of each, the galena-sphalerite and the pyritic-copper ore, respectively. In polished sections, relations are sometimes apparent that clearly indicate that the galena is later than the chalcopyrite and some of the pyrite.

These matters of the paragenesis, segregated occurrence, and zonal distribution of the ores tell a clear consistent story of the outward travel of the metal-burdened mineralizers and of their dropping first their copper and then their lead and zinc. In addition, and like an independent and supporting line of evidence, are the concomitant changes in the character of the country rock, stages in the alteration of the limestone.

### METAMORPHISM OF THE LIMESTONE

#### *Character of the Fresh, Unaltered Limestones*

Something has already been said of the black and white, *i. e.*, the fresh and the altered phases of the limestone. The former, on the surface, is a blue gray, pitted, faintly banded, and otherwise like the normal blue limestone common in Carboniferous horizons of the Southwest; underground it is often black as coal. In composition, these beds, on the western side of the camp, contain 15-98 per cent. lime-carbonate, and 0-85 per cent. quartz in the form of sand grains. In somewhat metamorphosed areas, the proportions of these materials are reduced by varying amounts of a third constituent, lime-silicate material. The magnesia content is very low; clay is almost entirely absent.

So pure are the prevailing quartzites of the region that in Bingham much material goes by the name of limestone that contains 20 per cent. or less of lime, the remainder being quartz sand. In these quartzites, the presence of 10 per cent., of lime carbonate is evident to the eye in a rock, which is less well cemented, more friable, more easily weathered, and which, perhaps, sustains a struggling reef of vegetation; whereas, the pure quartzites above and below the calcareous bed make bare slopes strewn with the fine, angular debris of weathering. It can be scratched with a pick point, wherefore, in the phrase of the camp, it is "limy." Gradations from limestone to quartzite are common and often abrupt in directions both normal and parallel to the bedding. Such transitions may be from a very pure type of the one to an equally pure phase of the other.

#### *Limestones not Silicified*

Unexpected, rapid, and seemingly erratic transitions from limestone to quartzite sometimes puzzled and baffled the miner in his attempt to follow "good lime." He was perhaps somewhat blinded by a preconception of beds of differing character and bedding planes as being parallel, never

ending and never meeting. At least, there arose a belief in the silicification of the limestones (the quartzites themselves are very fine-grained), a belief that has often been a convenient explanation for unexpected "siliceous" material and the sudden disappearance of "good lime."

But out of some 1200 thin sections from samples taken by Prof. A. N. Winchell and myself within the most productive and most highly mineralized and altered portion of the Highland Boy and Yampa Limestones, perhaps a half dozen were found, by Professor Winchell, to be to any considerable extent silicified. Many were "silicated;" in many, lime-silicate minerals were abundant; but there was no wholesale replacement by silica. In most cases where, to the eye, the classification of the rock as quartzite or limestone seemed difficult, the rock appearing smooth, hard and siliceous, a sufficient content of original quartz in the form of sand grains was found to justify its resemblance to and classification as quartzite. On the other hand, the lime-silicate rocks are ordinarily easily recognized once their acquaintance is made; and in Bingham the presence of abundant lime-silicate minerals usually denotes a considerable original lime content.

#### *Silication of Limestones*

The clear effect of intrusion on the limestones in Bingham has been their conversion *en masse* into silicate minerals, chiefly wollastonite, diopside, both brown and light-colored garnets. Other silicate minerals, including serpentine, actinolite, tourmaline, chlorite, and a peculiar lime silicate,

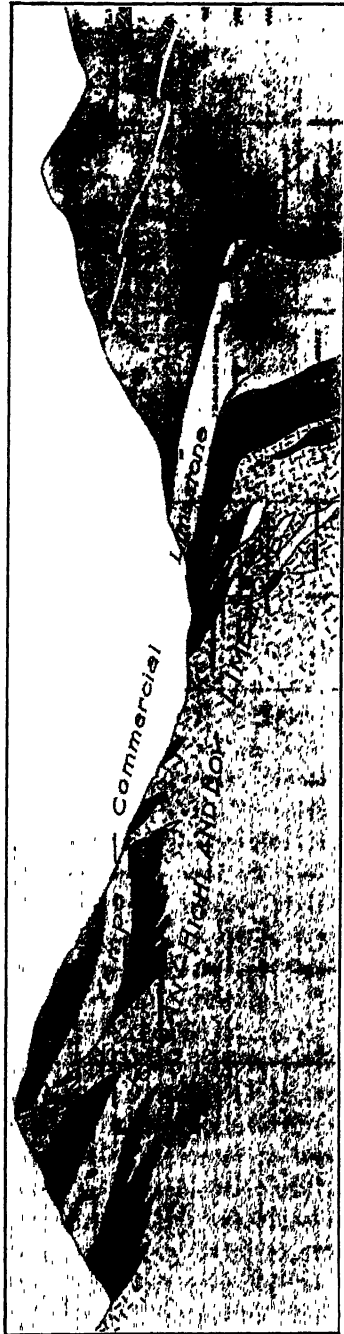


Fig. 9.—A GENERALIZED VERTICAL SECTION NORTHWEST THROUGH CENTRAL PORTION OF DISTRICT; SECTION A-A SHOWN IN FIG. 3.

provisionally called "Racewinite" by Professor Winchell, are found; but wollastonite, diopside and garnet are quantitatively by far the most important. These non-magnesium-bearing silicates reflect, in an interesting manner, the non-magnesian character of the limestones.

The net result of alteration has been the development of these lime silicate or white limestone areas, which extend 2000 to 3000 ft. from the central porphyry mass. This white limestone belt may properly be called the zone of contact alteration. It is not homogeneous in either its mineralogy or physical character. Just as the ores change in character so does the nature of the limestone alterations change as the distance from the larger porphyry area increases.

There are three distinct types of altered limestone:

1. Masses of limestone abutting the main mass of the porphyry or adjacent to larger apophyses, notably on the Highland Boy 800-ft., 1400-ft., 2000-ft. levels, are often converted into garnet, with which occur minor amounts of other silicates, including asbestos, serpentine, and tremolite; often, pyrite and specularite are abundant. Locally these areas are saturated with disseminated sulfide mineralization and become minable as ore. In the Highland Boy Limestone, many large bodies of copper ore occur in such garnetized and pyritized limestone. Such material is sometimes sandy in texture, soft, easily picked, and runs; but much of the garnetiferous material is hard and resistant.

2. In the outer half or two thirds of the white limestone zone are found large areas consisting almost wholly of diopside and wollastonite, forming a fine-textured rock, usually snowy white, and often horny and translucent in thin chips, which is most tough and resistant both to drill and pick.

3. In many places within the alteration belt, little more than recrystallization of the limestone has occurred, the black color being lost, and a soft white marble resulting. Possibly, simply marmorization is more common in the outer part of the alteration zone but I am not sure that such a generalization is justified.

In the outer margin of the white-limestone areas some details are interesting, and probably significant of the manner in which these changes are effected. Fissures, fractures, and bedding planes seem to facilitate alteration. For in this outer margin where the black limestone meets the white, are rocks beautifully banded, black and snow white, the bands, each one or more inches wide, following the bedding; frequently, white bands are connected along a cross-fracture or joint. Ribbons of white altered material may often be seen following prominent bedding planes. Sometimes distinct layers or streaks of garnet cut through marbleized areas or material containing wollastonite, diopside, and small amounts of other silicates. Narrow bordering zones of white, silicated limestone follow alongside dikes far into areas of black limestone. In

other words, the distribution of the white or altered material is often, in detail, precisely that which would be expected were these alterations largely the work of solutions or other agencies working along through the physical openings and lines of least resistance within the limestone.

#### RELATION OF THE LIMESTONE ALTERATIONS TO THE ORES

These alterations are independent of the ores, although they are unmistakably related in a broad way to the ore-forming processes. The limestone alterations are far more extensive areally and have been far more thorough and complete than has been the metalliferous mineralization. But the linear reach of the ores exceeds that of the alterations. In the "Leadville" country, lead ores occur 1200 ft. out in black limestone beyond the known white limestone. In the Utah Apex mine, lead orebodies penetrate considerable distances into the black limestone. On the eastern side of the camp, in the Bingham mines properties, much ore has been found along and within black limestones far beyond the range of the white-limestone zone in which occur most of the ores of the United States mines. On the north, in the region of Markham and Freeman Gulches, in the quartzite area north of and overlying the limestones, are small occurrences of both lead and copper ores in gray to black limestone beddings.

Although the mineralizing and metamorphosing processes operated within about the same areas, the latter reached out farther and spread back into the porphyry itself; but both, by their distribution, clearly point to the porphyry area as the locus of their origin and cause. In this, they are at least related in being probably more or less contemporary phases of a single intrusive process. The varying types of alterations and of ores presumably represent reactions determined more by conditions and place than by time.

From porphyry outward are: (a) copper, (b) mixed lead and copper, and (c) lead and lead-zinc ores; and (a) garnet-pyrite-specularite-tremolite-asbestos bearing, and (b) diopside-wollastonite and, to a lesser extent, garnet and other silicate-bearing rock and marbelized limestone; and (c) the black, unaltered limestone. In each, the limestone alterations and the ores are very likely recorded, a progressive change in a radial direction in the conditions surrounding the active intrusive, a change, presumably, toward lower temperatures and pressures. The fact of some such general change is unusually clear; on the western side of the district it is almost diagrammatic.

But that these several types of product and reaction are not rigidly distinct nor were long separated in time; or that the conditions producing them did not at any given point obtain long without change, seems to be clearly indicated by the fact that there are so many exceptions and



complications of the one type by another. Freakish nests, streaks, fissures containing galena and sphalerite and even sizable bodies of lead ore, are found even in the large copper replacement orebodies in the highly silicated areas near the porphyry. Sheets of massive lead and zinc sulfides occupy fissures within the porphyry. These in-lying occurrences of lead ores are, no doubt, correctly interpreted as broadly representing the back sweep during the closing stages of mineralization and intrusion of the marginal, lead-depositing conditions. Details of the paragenesis of the lead and copper minerals indicating the lead to be later seem to support this view. But in so far as these ores are the work of solutions serving as carriers, at any point at any time, either lead or copper ores would seem to have been potentially possible, if momentarily the proper conditions governing deposition of the one or the other metal were present. It is only an assumption that any such intrusive movement as this is a process that steadily approaches a climax of intensity and activity and then as uniformly subsides. It may as easily reach its climax through a series of spasmodic eruptions, and its subsidence may be interrupted by sporadic renewals of mineralizing, or even, intrusive activity, local perhaps, as regards the district as a whole. I know of no clear case of copper ore cutting lead ores in such a fashion as to indicate it to be younger; but think such an occurrence would be quite possible though rare.

Of course, in so far as these ores represent differentiation and segregation of materials at depth in the magmatic reservoir itself, whence they presumably come, the character of the ore (*i. e.*, lead or copper) may then reflect a definite stage in the intrusive process as a whole. But the differentiation seems more clearly to have occurred during transit; and to be, in effect, the reaction of the mineralizing agents to environmental changes as of temperature, pressures and materials. In no other way does it seem possible at once to explain their zonal distribution, their transitions within a continuous orebody from one type to the other, and their definite relation to the line marking the limit of metamorphic alteration in the limestone.

By way of summarizing some of these matters, it may be said that an almost diagrammatic situation in Bingham suggests the following theoretical conceptions and inferences:

1. The geographic distribution of the ores shows them to be, in some way, related to the monzonite intrusion.
2. The change from copper to lead ore in directions radial to the main and central porphyry area also evidences a genetic relating to the porphyry, and suggests a certain continuity and unity in the ore-forming process, whatever its nature.
3. The localization of lead ores in the vicinity of and beyond, and the restriction of copper ores within a definite line marking the limit of the white, or altered limestone, indicates the formation of the ores and altera-

tion of the limestone to be the work either of the same process or of more or less contemporary processes effected alike by conditions of temperature and pressure surrounding the intrusive.

4. The ore-forming processes had the greater scope in distance and probably in time, as they penetrated into unaltered areas of limestone and swept back into the porphyry itself.

5. The metasomatic character of the replacement of the limestone by copper ores and the detailed relations to bedding and fractures of the limestone alterations suggest the work of pervasive agents, such as solutions and gases.

These inferences lead to the following principles of mining and prospecting in the district:

1. Most of the ores occur within 2000 or 2500 ft. of the larger and central masses of porphyry. Beyond these limits, the greater the distance from these masses of porphyry, the poorer are the chances of finding ore.

2. Within the productive limits and outside of the porphyry area, the ores are confined within the mass of the thicker limestone formations, and to several thin overlying and underlying limestone beddings.

3. Fissures normal to the strike of the bedding may contain ore in the vicinity of limestone beds, but rarely elsewhere.

4. Copper ores are largely confined to white limestone areas nearer the porphyry; while outlying orebodies in black limestone are usually lead ores.

## Petrographic Studies of Limestone Alterations at Bingham

By A. N. WINCHELL,\* MADISON, WIS.

(New York Meeting, February, 1924)

IN CONNECTION with law suits between mining companies at Bingham, Utah, a few years ago, the writer made petrographic studies of more than 1400 rock and mineral samples in thin sections, and also careful studies of their field relations.

In petrographic studies, even when an area is studied intensively, attention is commonly centered very largely on the unusual features of special interest, so that the relative abundance of rock types (or minerals or textures) can only be determined by a study of map areas outlined largely by field methods, and cannot be based directly on microscopic work. It is very uncommon, and usually impossible, to take samples at regular short intervals along and across formations. It is precisely because such methods were used at Bingham that the work presents a rare opportunity for determining, on a *microscopic basis*, the relative abundance of rock types and the continuity of gradations between rock types. At the same time, a study was made of the alteration of sediments under the influence of igneous intrusions, with results that are believed to be of interest and importance.

### SANDSTONE-LIMESTONE GRADATION

The sedimentary rocks of the Bingham district are chiefly sandstones, with some beds of limestone, all now lying with their strike nearly east and their dip nearly north at an angle of about 30°, near the surface. The limestone beds are remarkably irregular in thickness in some places, but usually change very slowly in composition along the strike. However, the most interesting results are obtained from a study of a section across the beds at right angles to the strike. In some places, such sections show the usual alternation of pure sandstone with nearly pure limestone, in the simple manner assumed in most geological discussions.

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The condition, in some sections, through the "Highland Boy" limestone, however, differs widely from any such simplicity. As shown in Fig. 1, this limestone grades very irregularly and indefinitely into the sandstone that separates it from the overlying "Yampa" limestone. All sorts of proportions of quartz and calcite are found in this gradation and, instead of nearly pure limestone sharply separable from nearly pure sandstone, as illustrated by the relations between the Yampa limestone<sup>1</sup> and the



FIG. 1.—VARYING TENOR OF QUARTZ IN SAMPLES TAKEN AT 25-FT. INTERVALS ACROSS THE HIGHLAND BOY AND YAMPA "LIMESTONE" AND THE INTERVENING SANDSTONE AT BINGHAM, UTAH.

adjacent sandstones (in Fig. 1), the Highland Boy limestone *as a formation* locally consists of as much as 80 per cent. quartz; petrographically, such parts must be considered to be sandstones.

Of the total number of samples taken, 600 were found to represent essentially unaltered sedimentary rocks; 20 per cent. of this number were practically pure limestone. Calculating the amount of quartz in each

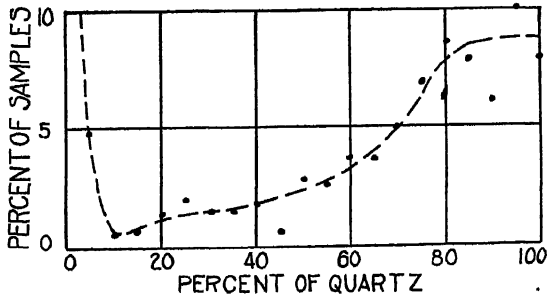


FIG. 2.—RELATIVE ABUNDANCE OF SEDIMENTARY ROCKS WITH VARYING TENOR OF QUARTZ AT BINGHAM, UTAH.

sample to the nearest multiple of 5 per cent., the relative number of samples of each type thus established is shown in Fig. 2. If the limit between limestone and sandstone were to be established in accordance with this diagram, it might well be placed at about 10 per cent. of quartz,

<sup>1</sup> In the Inland tunnel the Yampa limestone formation is also largely a calcareous sandstone. The Parnell limestone formation is likewise petrographically a calcareous sandstone in some places, for example, east of the Andy incline.

as such types are the rarest. The very existence of such a gradation between sandstone and limestone seems to be ignored in geological, and even in most petrographic, literature and no attempt to fix a limit in the series is known to the writer. The only limit that needs no special defense is 50 per cent. of quartz (and 50 per cent. of carbonate), on the basis of which any rock in this series is sandstone, if it is composed dominantly of quartz, and it is limestone, if it is composed dominantly of carbonate. On such a basis, about 30 per cent. of the limestone samples taken at Bingham contain more than negligible amounts (5 per cent.) of quartz; on the same basis, 75 per cent. of the sandstone samples contain more than 5 per cent. of carbonate, and 25 per cent. of them contain more than 25 per cent. of carbonate.

The sedimentary rocks of the Bingham district have been altered in various ways in consequence of igneous intrusion. Most of the sandstones have been converted into quartzites; some of the limestones have been recrystallized to marbles, and there are all gradations between the unaltered and the recrystallized rocks. However, the more important results of the intrusion (so far as the rocks are concerned) are those that have changed the mineral and chemical composition of the rocks. Lime-silicate rocks have been produced in abundance in a zone adjoining the intrusion.

#### ORIGIN OF LIME-SILICATE ROCKS

The origin of lime-silicate rocks is still under discussion. For the rocks at Bingham, there are three possibilities that may be considered. Such rocks might be formed: (1) by recrystallization of sandstone with addition of lime (some silica would necessarily be removed simultaneously); (2) by recrystallization (without any addition) of a rock containing both quartz and calcite (with elimination of the carbonate radical, and possibly, of other constituents); or (3) by recrystallization of limestone with addition of silica (with concomitant removal of the carbonate radical).

#### *Recrystallization of Sandstone Theory*

It is clear, from the stratigraphic relationships, that it would be difficult to account for all the lime-silicate rocks as due to recrystallization of sandstone with addition of lime, as it is often possible to prove that these rocks replace limestone, and not sandstone, in the geologic sequence. However, this evidence is not sufficient to show that some parts of the silicated rocks are not derived from sandstone. The evidence on this point is to be found in the nature of the solutions that caused the silication and in the thin sections of the rocks partly silicated. Solutions coming from magmas are naturally rich in silica, because magmas usually contain at least 50 per cent. silica, and the Bingham magma contained about 58

per cent., as shown by published analyses of the rocks formed from it. Furthermore, solutions coming from magmas are likely to contain even a higher tenor of silica than their source, for processes of differentiation commonly cause a concentration of silica in the residual liquid, as shown by the formation of aplites, pegmatites, and quartz veins from such sources. On the other hand, the Bingham magmas contained only about 6 per cent. of lime, and solutions escaping from it probably contained little, if any, lime, as shown by the same facts. Therefore, such solutions are not a reasonable source for large amounts of lime, nor are they suitable agents to remove large amounts of silica. Finally, in the thin

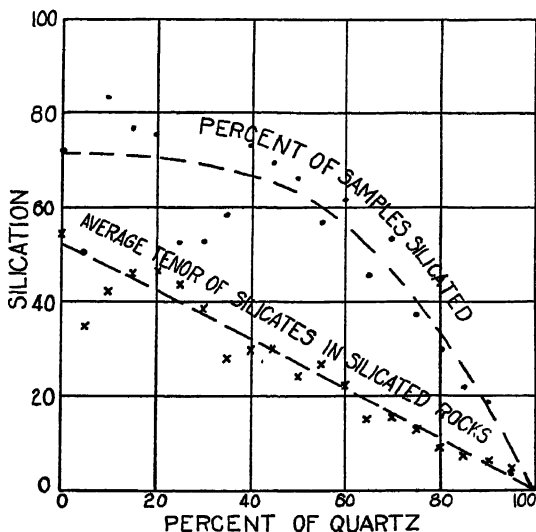


FIG. 3.—RELATIVE ABUNDANCE OF SILICATED ROCKS AND AVERAGE TENOR OF SILICATES IN THEM AT BINGHAM, UTAH.

sections of partly silicated Bingham rocks, no examples are found of progressive replacement of quartz by lime silicates, but, on the contrary, such silicates may replace a calcareous cement and leave the quartz grains unmodified. Microscopic study shows that more than two-thirds of the limestones (whether quartzose or not) collected at Bingham were more or less silicated, as shown in Fig. 3, while no pure sandstones were silicated at all, and calcareous sandstones only (as a maximum) to the extent of silication of the calcareous portion (see Fig. 3). For all of these reasons, it is believed that no part of the lime-silicate rocks at Bingham was derived from sandstone.

#### *Recrystallization Without Addition Theory*

If it is assumed that these rocks were formed by elimination of some constituents and recrystallization of the remainder, it is easy to calculate

the amounts of calcite and quartz necessary in the original rock to form any lime-silicate mineral, and leave no excess of either calcite or quartz. Assuming calcite and quartz present in proper proportions, the constituent eliminated to form wollastonite would be only carbon dioxide; if the original rock consisted of quartz and dolomite in certain proportions, elimination of the same constituent would permit the formation of diopside from the remainder. No other minerals found at Bingham can exclusively form a rock produced from a mixture of quartz and calcite (or dolomite) by elimination only of carbon dioxide. To produce (without introduction of new material) a rock composed essentially of any one or any mixture of the following minerals, all found at Bingham—apophyl-

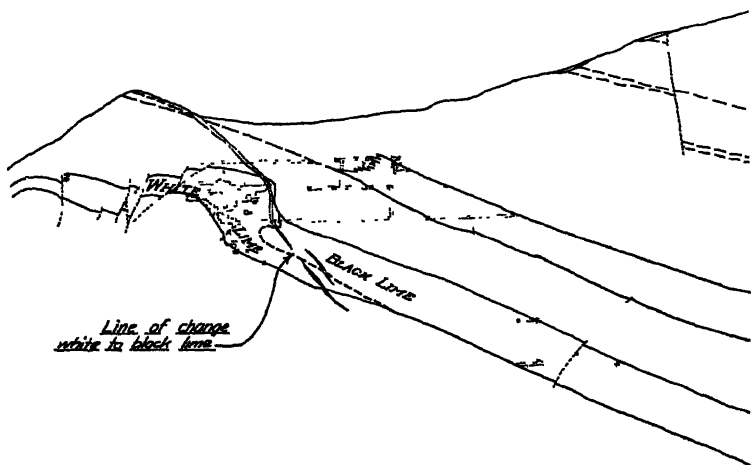


FIG. 4.—VERTICAL SECTION THROUGH THE HIGHLAND BOY LIMESTONE AND OTHER FORMATIONS AT BINGHAM, UTAH, SHOWING THAT SILICATION IS NOT ACCOMPANIED BY DECREASE OF VOLUME; THE "WHITE LIME" INCLUDES SOME LIMESTONE MERELY BLEACHED BY LOSS OF CARBONACEOUS MATTER, BUT MUCH OF IT IS LIME-SILICATE ROCK.

lite, chlorite, epidote, garnet, sericite, serpentine, tremolite, zoisite—would require elimination of other constituents, besides carbon dioxide, and elimination of such constituents on a large scale. A mixture of 37.5 per cent. of quartz and 62.5 per cent. of calcite could be converted into pure wollastonite by loss of carbon dioxide and recrystallization, and the process would involve a loss of 27.5 per cent., by weight, or more than 30 per cent. by volume. A mixture of 40 per cent. of quartz and 60 per cent. of dolomite could be converted into pure diopside by loss of carbon dioxide and recrystallization and the change would involve a loss of 29 per cent., by weight, and 44 per cent. by volume. That is, the theory of formation of lime-silicate rocks solely by elimination of constituents and recrystallization of the remaining portions would require a loss of 27 to 29 per cent. by weight and 30 to 45 per cent. by volume of the

original rock, *as minimum amounts*, and much larger percentages as maximum amounts.

The numerous vertical sections through the Highland Boy limestone and other formations, carefully worked out for the lawsuit, show that there has been no decrease of volume as a result of the change of the limestone to lime-silicate rock. One of these vertical sections is reproduced in Fig. 4. There is a greater thickness of the limestone formation in the region of silication and mineralization than elsewhere, so that one might be tempted to assume that silication was accompanied by introduction of so much new material as to cause *increase* of volume; but this conclusion is not warranted. The greater thickness is probably an original condition; and when the matter is investigated, in detail, on a smaller scale, it is found that there is no relation between silication and variations in thickness. The lime-silicate rocks of Bingham, therefore, were not formed by silication of limestone without addition of new material.

### *Recrystallization of Limestone Theory*

There is evidence in the mines that a given bed of limestone can be converted into lime-silicate rock with no important change of volume, as the thickness remains unchanged; and there is evidence in thin sections that an abundant calcite cement can be converted into lime-silicate minerals without change of volume. It is believed, therefore, that the change to silicates has occurred at Bingham with no important change of volume.

Assuming that materials present in the rocks are used in the new minerals, and ascribing to primary detrital quartz the largest portion of the silica of the new minerals that can be thus assigned without leading to change in volume, it may be calculated that:

Wollastonite-rock may be derived from about 10 per cent. quartz and 90 per cent. calcite.

Diopside-rock may be derived from about 43 per cent. quartz and 57 per cent. dolomite.

Garnet-rock<sup>2</sup> may be derived from about 15 per cent. quartz and 85 per cent. calcite.

Wollastonite is far more abundant than any other mineral in the lime-silicate rocks at Bingham; diopside is next in abundance, being much commoner than garnet, which is probably third. As these minerals form the bulk of the lime-silicate rocks, it is unnecessary to continue the calculations.

These calculations show how relatively unimportant would be the original quartz of the sedimentary rocks as a source of silica for lime-sili-

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<sup>2</sup> Grossularite-rock from about 12 per cent. quartz and andradite-rock from about 16 per cent. quartz.



cates on the most favorable assumptions, provided there is no change of volume. As a matter of fact, microscopic evidence shows that original quartz is not used (at least in all cases) in the formation of lime silicates, for in some thin sections the calcite matrix has been converted completely into lime-silicate minerals with no encroachment on the rounded outlines of the detrital quartz grains. It is, therefore, believed that lime-silicate rocks are formed by a combination of lime from the carbonate of limestone with silica from solution, the carbonate radical taking the place of the silica in the solution. In order to test this conclusion, as fully as possible, two sets of detailed examinations of the altered and unaltered sediments were made; the first of these was a study of the accessory constituents ("heavy residues") of the sediments to learn whether any one of them remained unaltered during silication and might therefore throw light on the nature of the original rock; the second was a study of the porosity of the sediments before and after silication to determine whether a marked change in porosity could be cited as an explanation of the absence of change of total volume.

### *Study of Heavy Residues*

Many rocks contain very small crystals or grains of uncommon minerals which are so sparsely distributed through the rock mass that they may be entirely absent from a thin section. Even if a grain or two are found in a thin section, it is not possible to get any reliable measure of their abundance from such a source. Therefore, to investigate these minerals, special methods are used which depend on the fact that they have higher specific gravities than the abundant constituents of the rocks. A large sample of the rock is crushed to a powder, which is sized by means of suitable sieves, and then each size is panned to eliminate the light minerals. In the "heavy residues" thus obtained, there is commonly a concentration of 10 to 100 into 1, and a mineral that was very sparse in the original rock may be abundant in the concentrate; in this way, it may be easily identified and its abundance measured.

Some of the heavier minerals are important and others are not. Thus, the sulfide minerals are deposited in orebodies and simultaneously may be scattered through the adjoining rocks, but, though of such great importance as ores, they are of little significance in the rocks, because they were introduced long after the formation of the rocks. In the non-igneous rocks at Bingham, the heavy minerals are not numerous; aside from the sulfides, zircon is the only one which is widespread. This mineral is hard, insoluble, and stable under a great variety of conditions. It has been shown<sup>3</sup> that it is formed by early crystallization in magmas, usually

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<sup>3</sup> J. D. Trueman: *Jnl. Geol.* (1912) 20, 248.



FIG. 5.—ZIRCON IN CONCENTRATE OF BINGHAM SEDIMENT CONTAINING 50 PER CENT. QUARTZ. ROUNDED TRANSLUCENT GRAINS OF VERY HIGH RELIEF ARE ZIRCON. AMOUNT OF ALL MATERIAL SHOULD BE GREATLY INCREASED IN ORDER TO BRING OUT A CORRECT COMPARISON WITH FIGS. 6-8.

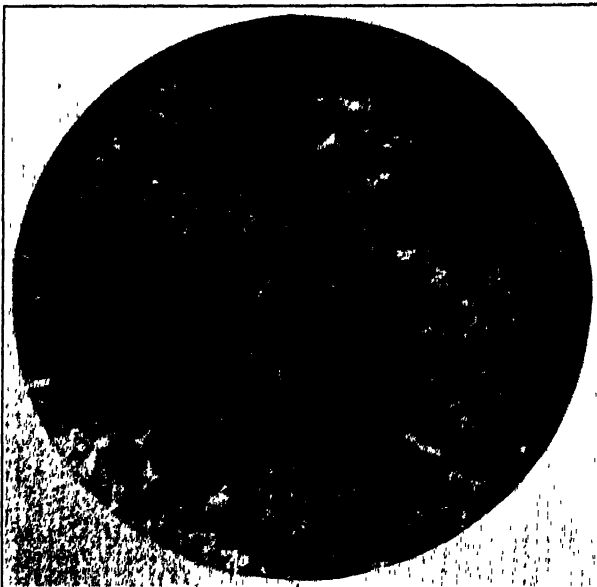


FIG. 6.—ZIRCON IN CONCENTRATE OF BINGHAM SEDIMENT CONTAINING 98 PER CENT. OF QUARTZ; ROUNDED TRANSLUCENT GRAINS OF VERY HIGH RELIEF ARE ZIRCON.

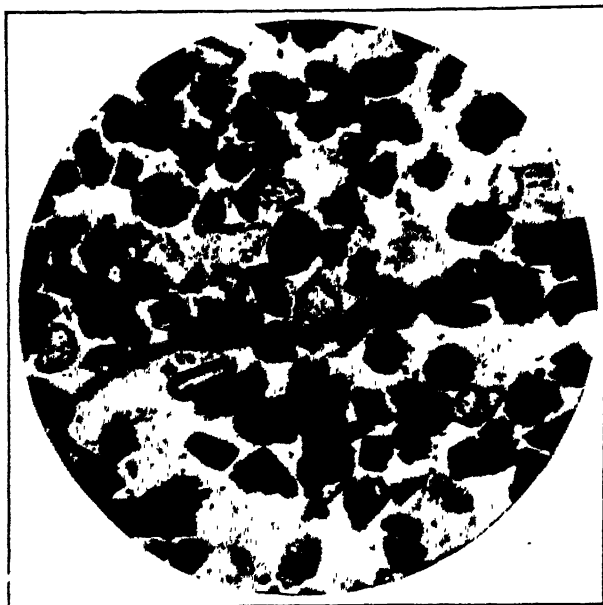


FIG. 7.—ZIRCON (AVERAGE AMOUNT) IN CONCENTRATE OF LIME-SILICATE ROCK FROM BINGHAM, UTAH; ROUNDED TRANSLUCENT GRAINS OF VERY HIGH RELIEF ARE ZIRCON.

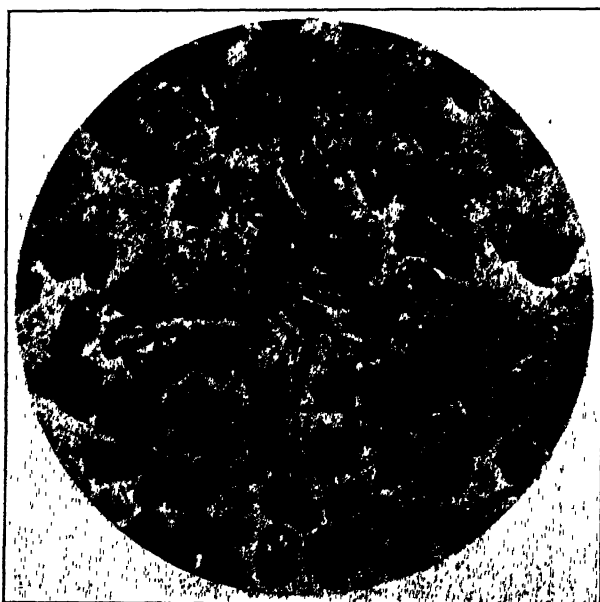


FIG. 8.—ZIRCON (MAXIMUM AMOUNT) IN CONCENTRATE OF LIME-SILICATE ROCK FROM BINGHAM, UTAH; ROUNDED TRANSLUCENT GRAINS OF VERY HIGH RELIEF ARE ZIRCON.

in well-defined crystals, and that it remains unaltered during the cooling of the rock mass; when the rock is broken up by weathering and erosion, it is rounded and surface-weathered but not destroyed; and, finally, that under the intense anamorphic conditions which change a sedimentary into a metamorphic rock it is unmodified, with rare and unimportant exceptions. The present study has proved that zircon is unmodified by the influences which produced the lime-silicate rocks.

These facts make it clear that zircon can enter the sedimentary rocks only as a clastic mineral (because of its insolubility); it is found widely, but sparsely, distributed in practically all detrital sediments,<sup>4</sup> and is not found in sedimentary rocks wholly produced by precipitation from solution; therefore, it is present in sandstones but not in most pure limestones. Its abundance in the sandstone-limestone series is approximately proportional to the amount of quartz in any given rock, though variations in its abundance occur in this series just as they occur in pure sandstones.

The Bingham rocks tested in this way yielded the following results, as obtained by A. H. Koschmann.<sup>5</sup> Some of the zircons recovered by him from these rocks are shown in Figs. 5 to 8, in which the relative abundance is approximately shown, except in Fig. 5.

#### A. ROCKS WITH KNOWN AMOUNTS OF ORIGINAL DETRITAL QUARTZ

PER CENT. OF QUARTZ	SAMPLE NUMBER	PER CENT. OF ZIRCON	PER CENT. OF QUARTZ	SAMPLE NUMBER	PER CENT. OF ZIRCON
98	952	0.0218	30	20	0.00063
98	14	0.0099	25	43	0.00225
75	42	0.00233	0	312	0.00000
60	208	0.00241	0	943	0.00000
50	44	0.00389			

#### B. SILICATED ROCKS

CONSTITUENTS	SAMPLE NUMBER	PER CENT. OF ZIRCON
Wollastonite, diopside.....	238	0.00382
Wollastonite.....	401	0.00172
Talc (?), diopside, calcite..	361	0.00041
Wollastonite, serpentine.....	389	less than 0.00027
Wollastonite, garnet.....	407	less than 0.00008
Diopside, serpentine.....	414	less than 0.00006
Serpentine, garnet, pyroxene.....	377	less than 0.00002
Serpentine, calcite.....	180	0.00000
Serpentine, diopside.....	249	0.00000
Diopside, wollastonite ..	265	0.00000
Wollastonite, diopside.....	291	0.00000
Diopside, serpentine...	426	0.00000

<sup>4</sup> Hatch and Rastall: "Petrology of the Sedimentary Rocks," 42, 192. London, 1913. Allen & Co.; P. G. H. Boswell: *Quart. Jnl. Geol. Soc.* (1915) 71, 536-591; see especially pp. 576 (and table), 578, 581, 584.

<sup>5</sup> Unpublished B. A. thesis, University of Wisconsin, 1919.

These results are shown graphically in Fig. 9, in which the rocks with known amount of original quartz are indicated by circles, while those of unknown percentage of original quartz are indicated by crosses. The latter samples (with the exception of 238 and 401) are plotted to indicate the maximum amount of quartz that can be assigned to them, assuming that they are derived from rocks similar to the former samples. Assuming that samples 238 and 401 were derived from rocks originally containing about 40 per cent. of detrital quartz, they take reasonable positions on the diagram. That is, this line of evidence indicates that ten of the twelve samples of lime-silicate rocks tested were derived from pure limestones or

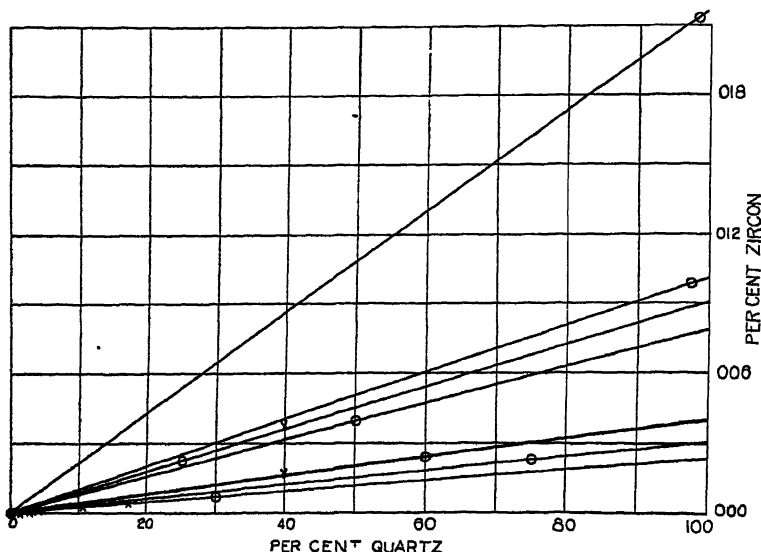


FIG. 9.—TENOR OF ZIRCON IN SAMPLES OF BINGHAM SEDIMENTS WITH VARYING TENOR OF QUARTZ, AND ALSO IN SAMPLES OF DERIVED LIME-SILICATE ROCKS.

limestones with only a little detrital quartz. Regarding the two other samples, the evidence is not at all conclusive; sample 401 may have been formed from a rock containing any amount from 8 to 57 per cent. of original detrital quartz, while sample 238 may have been derived from a rock containing any amount from 17 to 100 per cent. of detrital quartz; it is reasonable to believe that these rocks were derived from sediments containing 20 to 40 per cent. of quartz.

#### *Study of Porosity*

It has been shown that the rocks at Bingham were changed to lime silicates without any important change of volume. This refers to total rock volume, including pore space; therefore, it is important to learn whether these changes involved any important changes in the porosity of

the rocks. For this purpose, the porosity of twenty-three selected samples of Bingham rocks was determined by A. H. Koschmann, with the following results:

## A. UNSILICATED

PER CENT.

1 rock with 100 per cent. quartz has a porosity of .....	2.5
2 rocks with 75 per cent. quartz: 0.5, 9.6, an average of . . . . .	5.1
2 rocks with 50 per cent. quartz: 1.4, 3.3 .....	2.3
2 rocks with 25 per cent. quartz: 0.6, 2.7 .....	1.8
2 rocks with 0 per cent. quartz: 5.6, 6.8 .....	6.2

## B. PARTLY SILICATED

2 rocks with 25 per cent. quartz, 30 per cent. silicated: 2.4, 2.8 ...	2.6
2 rocks with 0 per cent. quartz, 25 per cent. silicated: 10.0, 18.3 . . . .	14.1
1 rock with 0 per cent. quartz, 50 per cent. silicated .....	2.6
3 rocks with 0 per cent. quartz, 75 per cent. silicated: 8.6, 0.5, 2.1 .....	3.7

## C. CARBONATE COMPLETELY SILICATED

3 rocks with 60 per cent. quartz, 40 per cent. silicated: 1.9, 4.4, 4.8 .....	3.7
1 rock with 25 per cent. quartz, 75 per cent. silicated .....	1.6
2 rocks with 0 per cent. quartz, 100 per cent. silicated: 3.7, 3.4 .....	3.5

In summary, the nine unsilicated rocks have an average porosity of 3.7 per cent., while the eight partly silicated rocks have an average porosity of 5.9 per cent., but the six completely silicated rocks have a porosity of only 3.3 per cent. The only rocks that show any important change of porosity accompanying silication are some of those with no quartz that have been silicated only in part. The original nature of these partly silicated rocks is indicated by the unsilicated residue to have been limestone (with or without quartz). The completely silicated rocks are quite uniformly less porous than the corresponding unsilicated rocks; therefore, they have not been produced by combination of original calcite and quartz with loss of carbon dioxide and consequent loss of volume; but by the combination of original calcite with new silica, the introduction of which has prevented loss of volume.

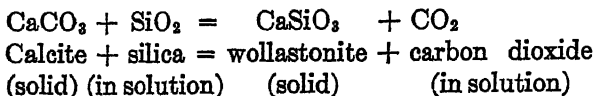
## PETROGRAPHIC HISTORY OF BINGHAM DISTRICT

The detailed study of the rocks of Bingham has disclosed many facts regarding their origin that should be brought together. The molten magma that forced its way into the sediments at Bingham did not solidify until it had reached almost to the surface, as it existed at that time. The temperature of such molten rock material near the earth's surface is known to be between 1200° and 1500° C. and it is known to contain large amounts of water in solution. This is the source of the heat, and the probable source of the solutions, that caused such profound changes in the rocks, and also produced the ore deposits. After the intrusion, the adjoining rocks were gradually raised to high temperature by conduction of heat and by means of heat transferred by moving liquids and gases.

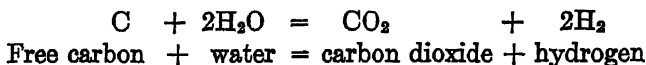
The important processes involving mineral changes followed in the order here given: (1) Silication and elimination of free carbon. (2) Mineralization and silicification: (a) Deposition of copper ores; (b) deposition of silver-lead ores. (3) Carbonation.

*Silication and Elimination of Free Carbon*

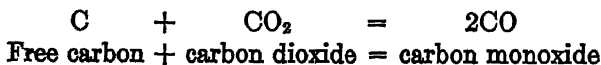
As already shown, the magmatic solutions at Bingham produced no important effects on the pure sandstones (probably caused some cementation, quartz enlargement, and recrystallization to quartzites), but produced marked effects on the limestones. The first change was probably that indicated by the equation:



The silica in the hot solutions combined with the lime of calcite to form solid lime silicate or wollastonite, while the carbon dioxide of the calcite went into solution. Another change of less importance may be expressed as follows:



This equation expresses the manner in which the free carbon that stains the limestone black may combine with the oxygen of water to form carbon dioxide and hydrogen. Both these equations result in the production of carbon dioxide; the first is inevitable if the solutions moved from the magma through limestone to the surface and contained silica; the second may have occurred, but at high temperature it does not absorb as much heat as the following, and therefore was probably prevented largely or wholly by the latter:



Furthermore, any activity of the kind shown by the second equation tends to produce more carbon dioxide, which tends to accelerate the third reaction, which, in turn, tends to inhibit the second reaction because it absorbs more heat and also because it tends to exhaust the free carbon.

The second reaction does not occur at temperatures below 550° C., and proceeds very slowly below 600° C., while the third reaction does not begin below 600° C., and is slow<sup>6</sup> even at 700° C., but proceeds freely at 800° and 900° C. These temperatures would be raised only a small amount by the pressure to which the whole area must have been subjected

<sup>6</sup> Rhead and Wheeler: *Jnl. Chem. Soc.* (1911) 99, I, 1153.

and also by decrease of concentration; it is safe to conclude that the free carbon was driven out of the limestones while the mass was at a temperature at least as high as about 700° C. The same solutions that drove out the free carbon produced the lime silicates that have been described. These include tremolite, which cannot be formed<sup>7</sup> at temperatures above 1000°–1100° C. Therefore, if these processes occurred simultaneously, the silication began at temperatures between 700° and 1000° C., and probably at temperatures near 800° C.

It should be noted that there was a great deal of silication accomplished during this period, which means that the solutions brought in a great deal of silica. At such high temperatures, carbonation is not impossible, but could only be accomplished under a pressure of CO<sub>2</sub> gas approaching one atmosphere, as CaCO<sub>3</sub> dissociates completely<sup>8</sup> to CaO and CO<sub>2</sub> to produce a pressure of one atmosphere of CO<sub>2</sub> at about 900° C. This process of dissociation of CaCO<sub>3</sub> begins at a much lower temperature and would continue at the lower temperature provided the CO<sub>2</sub> pressure was continually removed, as would be the case if hot solutions were continually carrying it in solution to the surface. Therefore, carbonation is almost impossible at the temperatures at which the silication began, and is improbable under conditions of upward-moving hot solutions even at considerably lower temperatures.

### *Mineralization and Silicification*

Silication of limestone by hot solutions containing silica may continue, though at a gradually decreasing rate, until the temperature falls<sup>9</sup> at least as low as 260° C. The microscopic evidence, as well as that supplied by the distribution in the mines, shows that most of the silication was completed before mineralization began, but the fact that ores are in some places intergrown with lime silicates proves that silication continued during at least part of the period of formation of orebodies. It has been shown<sup>10</sup> that the quartz of veins (not including pegmatite veins) crystallized at temperatures below 565° C.; therefore, the ores in the veins and replacements at Bingham were formed at temperatures below 565° and probably (at least in part) above 260° C. When the solutions cooled to these temperatures, they deposited the ores in veins and irregular replacement bodies. Boutwell<sup>11</sup> has described evidence that the ores were deposited at two periods; the earlier ores being valuable only for copper, while the later ores are chiefly valuable for lead and silver,

<sup>7</sup> Allen and Clement: *Amer. Jnl. Sci.* [4] (1908) 26, 101.

<sup>8</sup> John Johnston: *Jnl. Amer. Chem. Soc.* (1910) 32, 938.

<sup>9</sup> J. Koenigsberger: *Neues Jahrb. Bld.* (1911) 32, 101.

<sup>10</sup> F. E. Wright and E. S. Larsen: *Am. Jnl. Sci.* [4] (1909) 27, 421.

<sup>11</sup> J. M. Boutwell: Bingham Mining District. *Prof. Paper* 31, U. S. Geol. Surv. (1905) 210.



but also include some copper. However, all of these ores are alike in being siliceous, even when deposited in limestone; that is, much silica was deposited with the ores whether they formed in veins or as replacements of limestone; therefore, the solutions that deposited them were rich in silica. Furthermore, these solutions were not saturated with calcium carbonate, for they were able to dissolve large masses of limestone which were replaced by orebodies. Consequently, these solutions could not accomplish the carbonation described.<sup>12</sup>

Silicification differs from silication in distribution at Bingham, as the latter is confined to limestone beds (aside from some silication of calcareous quartzites) and is not found in the fissure veins, while silicification is found only exceptionally in the limestones, except where they have been replaced by ores, and is abundant in the fissure veins, and in the wall rocks immediately adjoining orebodies and veins.

### *Carbonation*

It has been shown that carbonation was well-nigh impossible during the period of silication and that the solutions that accomplished the work of mineralization were likewise wholly unsuited to produce carbonation. In general, carbonation is favored by low temperature, and it is evident that the hot solutions which produced the silication and mineralization at Bingham did not cause carbonation, unless they produced that effect after the period of mineralization, and when still further cooled. But even at that time these solutions would be coming from the same source and would probably still be charged with silica rather than calcium carbonate. It is more likely that the solutions which caused carbonation came from a different source—perhaps from the surface.

The evidence that carbonation did not precede mineralization nor silication is found in the facts already given; also in the fact that quartz grains of a calcareous quartzite have been found to be replaced by carbonate, while the calcite cement has been converted into lime silicate. If the carbonation had preceded the silication, there is no reason why cement and carbonate replacement material should not both be converted to lime silicate. But if silication preceded the carbonation, the silication would affect only that portion of the rock (the cement) which was calcite, and the carbonation would later affect only that part of the rock (the detrital grains) which was quartz. Again, carbonation of a pure quartzite is unknown, even in its beginnings, but secondary calcite forms tiny veinlets cementing fractures in such rocks as well as similar fractures in ores. Further, carbonation does not result in replacement of lime-silicate minerals, but fractures in such rocks are cemented by calcite in some

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<sup>12</sup> Compare J. J. Beeson: *Trans.* (1916) 54, 356.

cases. The only fact observed that suggests carbonation earlier than silication is the occurrence of some lime silicates in veins; some of these were surely produced directly as veins, and it is possible that all of them were so produced. If any of them represent silication of veins filled with calcite, this calcite was probably introduced before the period of high temperatures caused by the igneous intrusion. They imply deposition of calcite from circulating waters, but do not imply solution of quartz nor replacement of quartz by calcite.

### CONCLUSIONS

1. In the Bingham district, there is a complete gradation between sandstone and limestone, and the carbonate portion of these rocks shows all stages of completeness of transformation to lime silicates.

2. The rarest original sedimentary rock types at Bingham are composed of about 10 parts of quartz to 90 of carbonate.

3. About one-third of the limestone at Bingham contains an appreciable tenor of quartz.

4. About three-fourths of the sandstone at Bingham contains more than a negligible tenor of carbonate, and one-fourth contains upwards of 25 per cent. of calcite.

5. The lime-silicate rocks at Bingham were not produced by direct conversion of sandstone into silicate, nor by carbonation of sandstone followed by silication, as carbonation did not occur until long after silication.

6. The lime-silicate rocks were not formed from quartzose limestone (or calcareous sandstone) by recrystallization without addition of substance, as this would result in marked change of volume, which is not found.

7. The lime-silicate rocks were produced by recrystallization of limestone (including some quartzose types) with no important change of volume (or of porosity), and the loss of carbon dioxide was balanced by the introduction of silica, with magnesia in some cases. This conclusion is supported by all the evidence gathered from an examination of the field relations, a study of many thin sections, and special studies of porosity and of heavy residues.

8. The magmatic solutions at Bingham caused elimination of free carbon from the limestone, probably by converting it into oxides.

9. Elimination of free carbon probably occurred at temperatures above  $700^{\circ}\text{C}.$ , while silication was produced at temperatures below  $1000^{\circ}$ – $1100^{\circ}\text{C}.$ ; if these processes occurred simultaneously the temperature was probably between these limits.

10. Mineralization and silicification took place after the silication and at considerably lower temperature.

11. Carbonation occurred at still lower temperatures and was probably due to surface rather than magmatic waters; it is probably still in progress.

## DISCUSSION

WALDEMAR LINDGREN, Cambridge, Mass.—At that same time the Utah Apex Co. took a number (twelve, I think) of continuous groove samples across the Highland Boy and the Yampa limestone, which were assayed in order to ascertain whether there was any mineralization in the average. Large parts of the limestone were black, like quartzite, while other parts were white and altered by contact metamorphosis. The comparisons based on those analyses showed specifically, so far as the Yampa limestone was concerned, that there was considerable introduction of silica; say, the original limestone would contain 20 to 25-per cent. of silica and the recrystallized limestone would perhaps contain 35 to 40 per cent. But the most interesting feature was that the analysis showed a definite introduction of magnesia, the magnesia having increased consistently 3, 4, or 5 per cent. in the white or altered limestone. There was also evidence of the introduction of alumina; perhaps not nearly so conclusive as in the case of magnesia, but still worth noting. Besides, the complete elimination of carbon and the introduction of say, on the average, 4 or 5 per cent. of pyrite; the introduction of copper could not be detected in the average samples thus taken.

A. C. SPENCER, Washington, D. C.—How was the carbonaceous material eliminated in the process of hydrothermal metamorphism? The author suggests that it was eliminated after being oxidized.

WALDEMAR LINDGREN.—I do not know anything about it, except that the carbon is gone. The change from the black limestone to the white is sudden and usually takes place within a few feet.

A. C. SPENCER.—Considerable areas at Camp Ely, Nev., that were originally carbonaceous, are now occupied by limestones which, in their natural state, when struck by the hammer, emit a fetid odor. At present those great masses of limestone are white, they have no graphite in them; the carbonaceous material has been eliminated.

My opinion has been that they had been swept out by heated waters and that, in the main, had been accomplished through change of these hydrocarbons perhaps into petroleum substances. The suggestion that that carbon had been eliminated through having been converted into carbon dioxide has been quite a surprise to me.

A. C. LAWSON, Washington, D. C.—One interesting point about the relationship of the black limestones to the white limestones of Bingham is that in the vicinity of the intrusive masses the limestone is white, far away from them it is black, and in the intermediate zone it is both white and black. The limestones are rather thin bedded and for considerable distances (that is hundreds of feet) there are very narrow interleafings

of white limestone with jet black, that interleaving following the stratification. Whatever may be the process, there is a control of structure in some way that determines the change of black to white along the planes of stratification, and yet the boundary between the white and the black in a single stratum is of knife-edge sharpness. The black and the white beds alternate so that they have a glaring ribboned or striped appearance in the mine.

In this expression of opinion as to origin of the changes, there is an assumption that the process of change was contemporary with the molten condition of the magma. It seems far more probable that these changes continued long after the intrusive mass had solidified. We should not be so ready to assume that these changes are contemporary with the molten condition of the intrusive mass, but allow for considerable change after solidification, by reason of the effect of heat on the waters. As the mass at the time of solidification is very hot and it takes a long time to cool, there must be an important influence of that hot mass on the surrounding country in heating the ground water, in promoting circulation, and in the distribution of heat by this circulation.

WALDEMAR LINDGREN.—I am a little in doubt about the use of the word "hydrothermal" waters. If any distinction at all is drawn between the different waters, I would say that they were waters of a hotter temperature than those usually characterized as hydrothermal. In hydrothermal alteration of limestone, the tendency is toward the development of fine-grained silica, whereas here the tendency is toward silication—to develop into silicates. I should be inclined to draw a distinction between those two.

A. C. LAWSON.—If such a rock as the sandstones at Bingham Canyon were invaded by a laccolith of monzonite, I do not see how you are going to escape the conclusion that the temperature effects must have been conveyed to the contained water; that there must have been different densities of waters at different distances from the intrusive mass, and an induced circulation of meteoric waters. There is no escape from recognizing that something happened in that way. To say that all the water came from the magma and to deny any effect whatsoever of the induced circulation of meteoric waters ordinarily contained in the earth's crust, is carrying the theory too far. The notion that the heated waters in the sandstones may be effective for mineralization seems to be the most rational thing in the world. I do not deny the escape of volatile substances from magmas, but I do think the meteoric waters in the earth's crust must have important effects if you recognize that the action may go on long after the mass of the intrusion has solidified, and by reason of shrinkage and cracking has become permeated with those same waters, so that they may extract the metals.

RENO H. SALES, Butte, Mont.—There is unquestionably a spreading of this white zone of alteration outward and away from the intrusive rocks. The change from black to white lime has been effected principally by solutions. The first attack of these solutions on the limestone seems to have been partly chemical and partly physical. The structure of the rock is destroyed, causing it to crumble to a soft sandy material, retaining, however, its original black color.

This type of alteration is particularly prevalent where solutions have attacked the limestone at distances of several hundred feet from the igneous rocks. Where the limestone has been intensely shattered so that the solutions could circulate freely around the blocks and fragments, the above type of alteration has resulted in a complete collapse of the lime bed into a jumbled mass of lime blocks and black sandy material. A notable example of this type of alteration occurs in the Yampa limestone on the Apex 1300-ft. level.

It would be interesting to know what chemical change took place that caused this breakdown of the internal structure of the limestone.

F. L. HESS, Washington, D. C.—Is there any concentration of the carbon anywhere?

RENO H. SALES.—There is no concentration of the carbon observable to the naked eye.

A. C. LAWSON.—Does anybody know whether it is really in the form of carbon or in the form of bituminous matter?

RENO H. SALES.—I do not know. I only refer to the black discoloration of the limestone itself, which coloring remains until after it has collapsed down into a sand.

W. L. CUMMINGS, Bethlehem, Pa.—When reading discussions of this nature, I have wondered if any careful observations have been made as to the effect of molten slag on limestone. Molten slag approximates, to a certain extent, molten rock and it is well known that some slag dumps are hot in the lower portions for some years after the slag has been dumped.

I have been informed, by a former chemist of Bethlehem, that some years ago when walking over a large slag dump he found small fumaroles with a slight mineral deposition still going on although the slag had been dumped 2 years before. Conditions were therefore somewhat similar to those that occurred in igneous intrusions.

At some favorable point, it might be possible to analyze a limestone before slag had been dumped on it and afterward to analyze a contact specimen. With an analysis of the slag at hand, something might be learned as to the actual effect on the limestone near the contact.

A. C. LAWSON.—On Mt. Vesuvius, limestone fragments have been exposed to high temperature and hot gases in cracks of the lava. When

these were removed after a few weeks, beautiful new crystals were found upon the limestone. So the limestone experiment is to some extent being carried on at Vesuvius.

JAMES F. KEMP, New York, N. Y.—We must be careful to draw somewhat of a distinction between dry fusion and the fusion of igneous rocks, rich in vapors. In our experience with contact zones, we are impressed by two things; the first is their failure sometimes to appear in places where we would naturally look for them; and the second is the enormous extent to which they are developed in other places. By our experience we have also learned that the basic rocks are rather poor contact-zone producers; while the acidic rocks in which we customarily think there are larger amounts of dissolved gases, particularly hydrogen and oxygen, chlorine and fluorine, boron and carbon dioxide, are the most efficient agents.

A. N. WINCHELL.—The black coloring matter of the Bingham limestones is believed to be carbon because it is not volatile nor soluble in hydrochloric acid, but may be oxidized slowly at high temperature, as shown by the fact that the powdered rock when dissolved in acid leaves a grayish black residue which can be driven off slowly in the oxidizing flame at high temperature.

The writer knows of no simple proof that the solutions which caused the changes in the rocks came from the intrusive magma rather than from the quartzite, and he was careful to state in the paper that the magma was the *probable* source of the solutions. He is still of that opinion for (among other reasons) he considers that an intrusive magma gives off liquids and gases practically continuously until completely solidified, and the very first wave of these fluids would drive out all or most of the water present in adjoining rocks.

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## Some Geological Features and Court Decisions of the Utah Apex—Utah Consolidated Controversy, Bingham District

ORRIN P. PETERSON, BROOKLINE, MASS.

(New York Meeting, February, 1924)

THE decision of the Supreme Court of the United States not to review the findings of the lower courts closes an interesting chapter in the mining litigation that has arisen as a result of the extralateral feature of the mining law. The time seems opportune to record some of the important geological features, and also some of the legal features, of the controversy, in the hope that these will be permanently accessible to members of the mining profession.

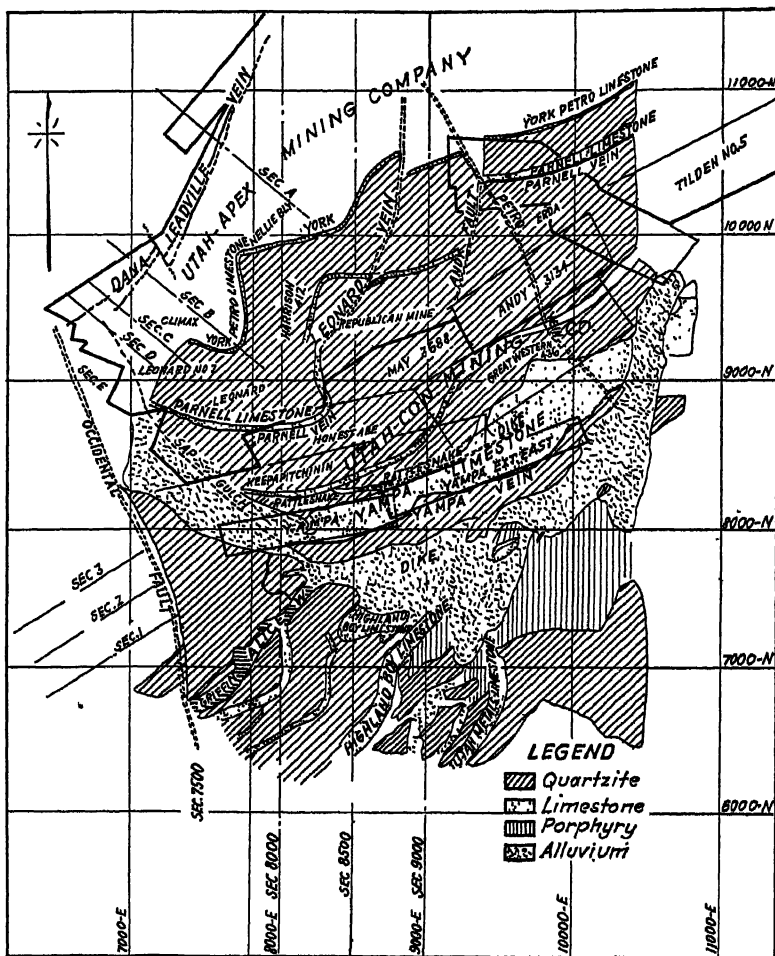
After many rumors of litigation, the Utah Consolidated Mining Co. sued its neighbor for the ore that had been, it was alleged, wrongfully extracted from its so-called Yampa limestone lode. This ore lay beneath Utah-Apex surface and was claimed by virtue of the extralateral rights conferred on the Utah Consolidated Co. through the ownership of certain specific mining claims, one of the principal claims being the Yampa. Previous to bringing suit, the Utah Consolidated Co. had strengthened its position by purchasing the Old Yampa mine and by making an agreement with the Utah Metal & Tunnel Co., which gave it clearer title to the outcrop of the Highland Boy limestone.

Access to the workings of the Utah-Apex Co. was secured and reciprocal privileges gave Utah-Apex representatives the right to enter the properties of the Utah Consolidated Co. This resulted in the Utah-Apex immediately bringing countersuit for ore alleged to have been wrongfully extracted from under its surface in the Leadville country, see Fig. 4.

Six cases came up for consideration: five related to the original suit and the countersuit, and one related to the Dana extralateral claims of the Utah-Apex Co.

Well-known attorneys, geologists, and mining engineers were engaged by both sides, and thousands of feet of development work were done to prove or disprove ideas that would sustain the contentions of the opposing sides. Models of wood, wire, and glass were constructed to present clearly to the court the actual physical relations. These models were also of great value to the attorneys and witnesses in clarifying hazy impres-

After the cases had been postponed, to allow for more adequate preparation of exhibits, the first case was brought to trial, before Judge Tillman D. Johnson, of the United States District Court for the District of Utah, early in November, 1919.



A number of cases, particularly, the Eureka-Richmond and the Lawson, or Kempton, had been previously decided and it had become evident that a limestone bed which was mineralized throughout would probably be held as a lode in the legal sense. The question to be decided was: Did the evidence show that the limestones were mineralized



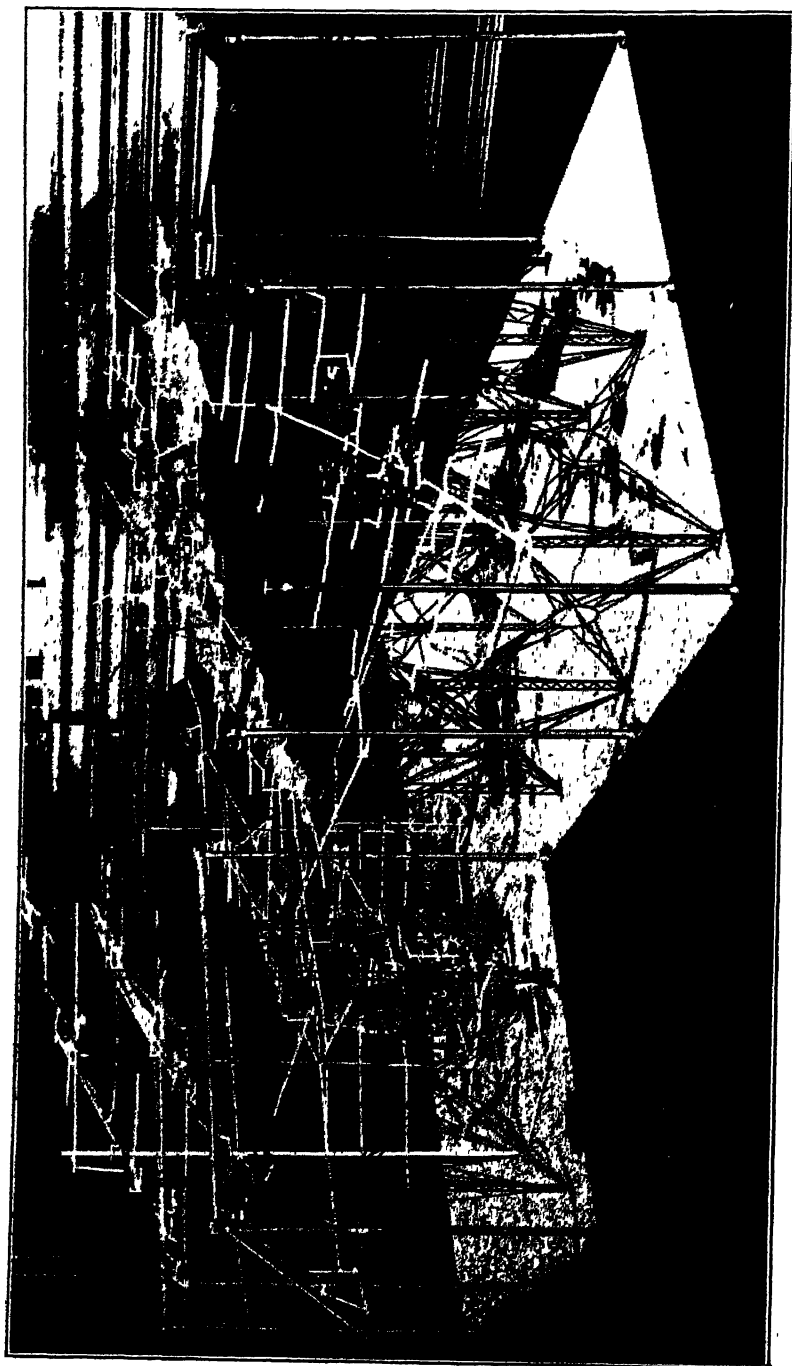


FIG. 2.—YAMPA CASE MODEL.

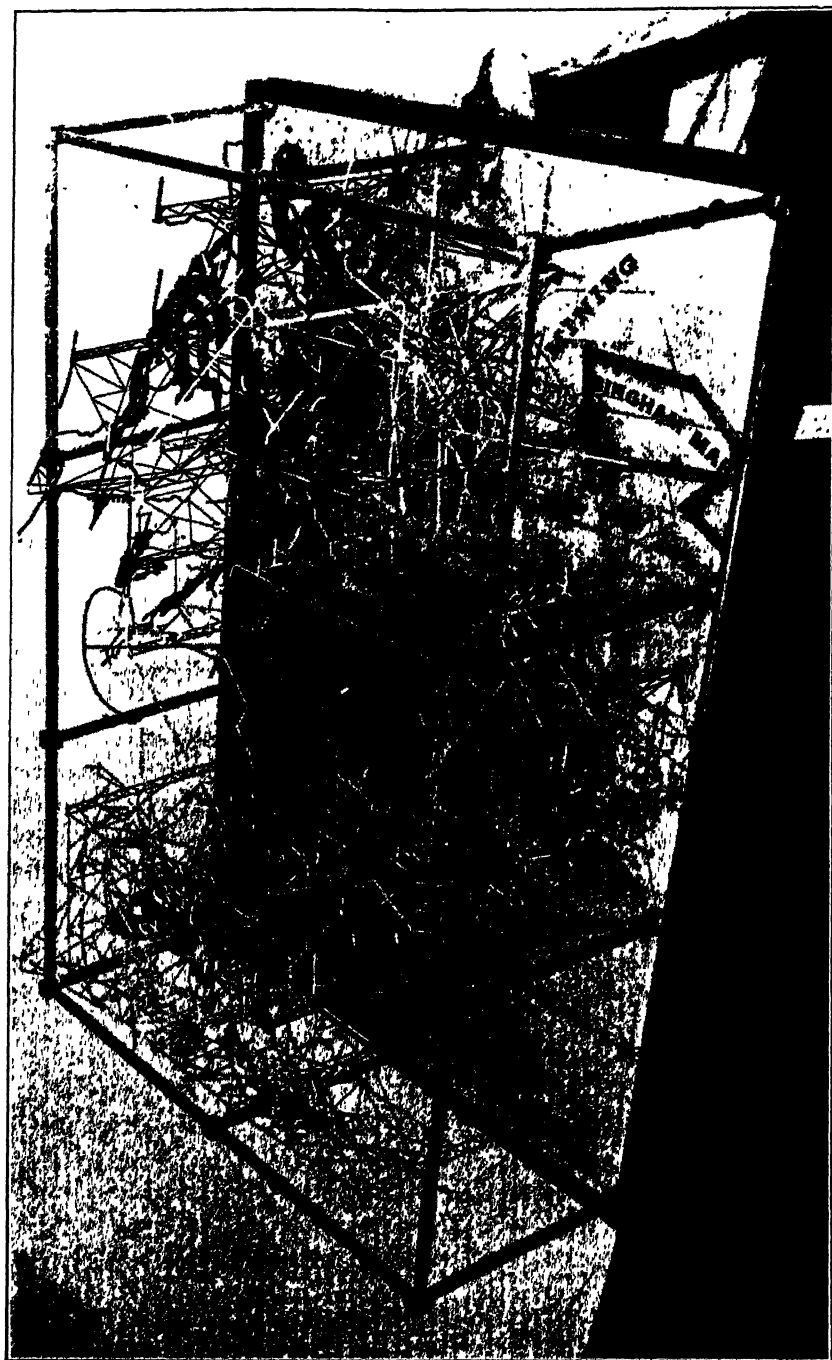


FIG. 3.—HIGHLAND BOY CASE MODEL.

throughout sufficiently to be thus classed as lodes. If the Highland Boy lode extended to the Leadville country, it included the Leadville orebodies; while if the Yampa limestone was a lode, it included the Utah-Apex orebodies in that limestone. Witnesses on the same side did not always agree; but apart from some differences of opinion as to what was quartzite and what was limestone, in certain important localities, the geological facts were evident and unusually close agreement among the witnesses was noted.

To bring absolutely incontrovertible evidence as to the amount of metallic sulfides in the rocks, in certain localities, the Utah-Apex Co. took many carefully cut channel samples and had the metallic contents determined by assay and analysis.

If the contentions of the Utah Consolidated Co. had been sustained by the court, it would have been a short jump to maintain in a mining district, and under somewhat similar conditions, that any rock formation could be considered a lode legally, as the rock limestone could hardly be supposed to have any inherent right to be exclusively considered as the only rock entitled to such consideration. The extralateral sweeps were such, and the claim rights such, that a decision construing the limestones as lodes would give the Utah Consolidated Co., by virtue of surface ownership of outcrops, practically all of the ore mined by the Utah-Apex Co. from the Yampa limestone and would confirm them in possession of the Leadville ore.

The trial lasted until Dec. 13, 1919, and the arguments of the attorneys were presented Jan. 29-31, 1920. The decision of the trial court was dated Oct. 20, 1920, and all cases, except the Dana extralateral, were decided in favor of the Utah-Apex Mining Co. The Utah Consolidated Co. at once appealed from the decision of the district court and the appealed cases were argued in Denver before the Circuit Court of Appeals. The decisions of this court were also in favor of the Utah-Apex. An attempt was then made to carry the fight to the Supreme Court of the United States, but this court refused to review the findings of the lower courts.

#### GENERAL GEOLOGICAL CONSIDERATIONS

The following succession of rocks is found in the Bingham district. Extrusive, mainly andesite; intrusive, mainly monzonite porphyry; limestone, lenses and members in quartzite; quartzite, known as Bingham quartzite. With the exception of the extrusive, all the rocks in the succession are known in the mines of the Utah-Apex and Utah Consolidated companies.

The Highland Boy limestone lies stratigraphically below the Yampa limestone and is separated from the Yampa by 300 ft. of quartzite, with included thin limestone beds.

The cases naturally divide themselves into two groups; the first concerning orebodies in the Highland Boy limestone and the second concerning orebodies in the Yampa limestone.

## MINING GEOLOGY OF OREBODIES IN HIGHLAND BOY LIMESTONE

### *General Considerations*

The detailed succession of rocks adjacent to the Highland Boy limestone, beginning with the top formation, is as follows:

Quartzite, 200–300 ft., includes two or more thin limestone beds near the top

Highland Boy limestone, 100–300 ft. thick, with several included beds of quartzite

Quartzite, 000–150 ft.

Limestone, 20 ft. of variable rock

Quartzite, 000–100 ft.

Utah Metals limestone, 80 ft. of alternating quartzite and limestone beds

Quartzite, 100 ft.

Limestone, 5–10 ft.

Quartzite, 150 ft.

Limestone, 5–10 ft.

Quartzite, 100 ft. plus.

A well-defined quartzite band occurs in the Highland Boy limestone near the top of that member; see Fig. 13. This band carries about 80

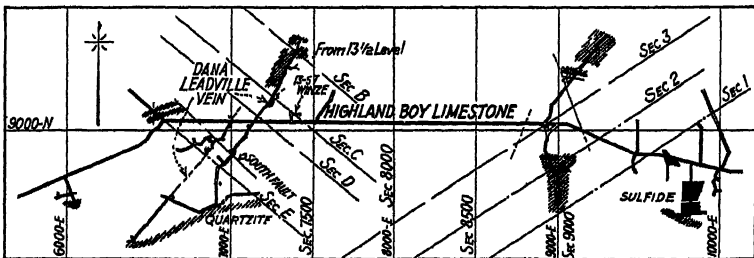


FIG. 4.—GEOLOGICAL MAP OF UTAH CONSOLIDATED 1300-FT. LEVEL.

per cent. of sand grains, the remaining material being calcium carbonate cementing the clastic particles. The color is greenish and the rock is finer grained than the thicker bands of quartzite. This quartzite, which has an average thickness of 30 ft., deserved more attention than it received during the trial, since ore made in it in large quantities on the 4C level, Utah Consolidated. The upper portion of the Leadville ore occurs between this quartzite and the overlying quartzite and is separated from the main Highland Boy orebody, on the ninth level, by the band of quartzite mentioned as well as by a second calcareous quartzite band.

Monzonite porphyry intrudes the sediments and occurs generally throughout the area described, but with a marked decrease in abundance as the distance from the Bingham monzonite core increases.

Throughout the principal ore-producing area of the Highland Boy limestone, the formation dips to the north at about 30°; up the dip, the formation is thrown into a succession of minor rolls so that the top of the limestone, in Utah-Metals ground, is at about the same elevation as the top in Highland Boy ground, to the north. Down the dip, the formation steepens and becomes practically vertical; the west end of the Consolidated 1600-ft. level shows a low dip to the north while the central and eastern portions of that level show steep northerly dips. The strike changes from south of east, in the eastern portion of the mine, to south of west in the western portion.

A number of faults, of comparatively minor importance, dislocate the various beds at intervals. A number of fissure veins, with trend approximately parallel to the main porphyry mass, cut the formations; they increase in number as the porphyry contact is approached.

#### *Outcrop of Highland Boy Limestone*

The outcrop of the Highland Boy limestone is not a simple one but is complicated by porphyry intrusions and by minor folding as well as by being covered, in certain localities, by alluvium. From east to west, the first definitely correlated area begins on the Omaha and Lorena claims and extends westerly from near the portal of No. 7 tunnel to where interrupted by faulting and folding, the result being to throw the outcrop southerly about 300 ft. Portions of this occurrence extend to ground covered by the Henry M. and Highland Boy claims. The dislocated portion of the outcrop occurs on the Troy, Sunset, Washington, Miner's Home, and Highland Boy Fraction claims. Two small occurrences southerly from the Seek-No-More portal may be Highland Boy limestone. The limestone at the Mountain Mayd portal is correlated as Utah Metals limestone.

An anticlinal fold is found near the intersection of the Highland Boy limestone and the Occidental Fault.

#### *Highland Boy Limestone Underground*

Three principal varieties of rocks are included in the limestone underground: A white altered rock that may be either limestone or marble, limestone altered to a rock in which lime silicates predominate, and unmetamorphosed blue-black limestone.

The rock that encloses the orebodies of the Highland Boy copper zone usually consists of all gradations between the white limestone and the silicate rock; at no point does the black limestone come in contact with

the ore. Various beds of quartzite occurring within the limits of the limestone have not everywhere been differentiated from the limestone.

A great block of black limestone, almost entirely unaltered and unmetallized, separates the two horizons—the Highland Boy and the Leadville. Except for an occasional fracture, this ground, the central portion constituting a zone about 1000 ft. in width, is unmetallized and unbroken.

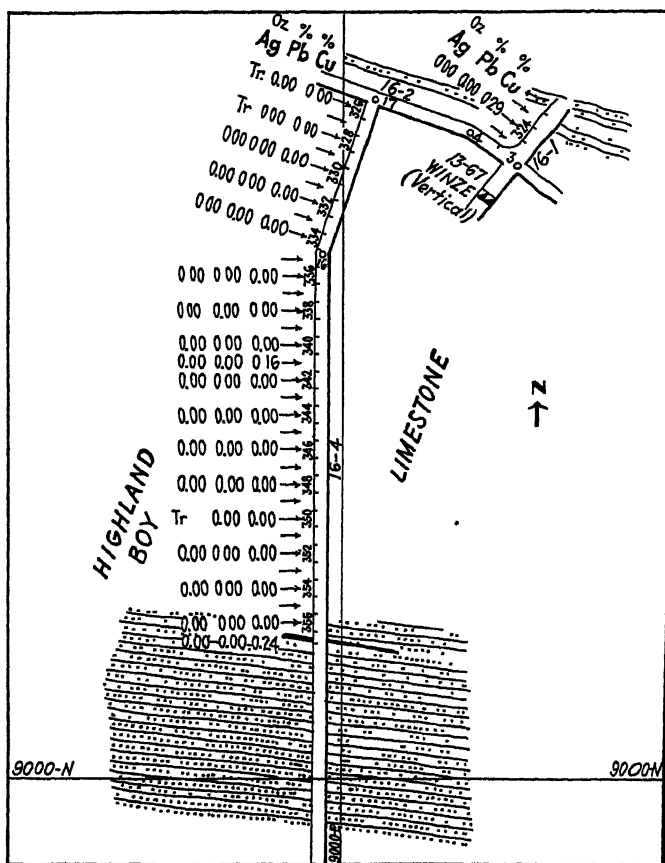


FIG. 5.—UTAH CONSOLIDATED 1600-FT. LEVEL.

The normal white limestone may be almost completely devoid of metallic sulfides, as is the condition on the 1600-ft. level, Utah Consolidated, in the crosscut southerly from a point a short distance west of the 13-67 winze. Out of thirty-five samples from the base of the limestone to the base of the first thin overlying quartzite bed only five samples showed copper and the content ranged from 0.05 to 0.29 per cent. Not one sample carried a trace of lead (see Fig. 5).

From the long northwest crosscut, Consolidated seventh level (see Fig. 6) eighty-one samples were taken. Of these, twelve carry copper up to 2.00 per cent.; only two samples carry lead and both are under 1.80 per cent. These samples were taken across the entire limestone less than 400 ft. westerly from the great copper stopes and show clearly the barrenness of the formation close to the most intense metallization.

### *Highland Boy Copper Oreshoot*

The tremendous ore zone that made the Highland Boy mine famous rakes northeast at an angle approaching 30°. The length of the mineralized area is nearly 4000 ft., its greatest thickness about 400 ft., greatest width 1200 ft., and the vertical range of the ore mined more than 1000 ft. This zone probably contained more than 50,000,000 tons of heavily mineralized ground, a considerable portion of which was too lean to mine.

The copper content of the lode has been variable; the zone of secondary sulfide enrichment has produced the principal portion of the profits won from mining. The orebodies of the northeast, or lower portion of the zone, are low in grade and the tonnage of commercial ore small. Possibly an average figure for the copper content of the orebodies of this portion of the mine would not exceed 1.40 per cent.

It is obvious that the intruded formation, in proximity to the central Bingham monzonite core, was shattered and fissured to a remarkable extent. The entire mass of the ore zone may be considered as the replacement of the main body of the limestone, not only in the fissures, or veins, themselves, but in more or less shattered and crushed limestone between the veins. This eastern area might be termed a zone of penetration into which the metallizing medium moved *en masse*. That any of these sulfides, except possibly near the porphyry, were fluid or molten and non-aqueous, seems difficult to visualize, but perhaps there is a somewhat different conception of its flowing through the weight of the superincumbent material while in a partly mobile condition. Doubtless this is a factor in all dike movement but the nature of the penetration here, especially the replacement of the country rock, argues for a more mobile condition.

A conspicuous set of veins parallels the periphery of the porphyry; a second set strikes about parallel with the strike of the limestone and dips usually somewhat more steeply to the north than the bedding. Fissures with other strikes and dips are of minor importance. On the Consolidated seventh level, the metallization has extended into the quartzite below the limestone but only locally has this ore been of sufficiently high grade to warrant mining.

The commercial metallization of the Highland Boy lode has been localized below an east-west trending dike which dips steeply to the north.

In places, this dike splits and the included limestone masses have been replaced by ore, but at no place has ore in quantity been removed from the north side of the dike. One unprofitable stope, from which 100 tons were removed during exploration, occurs north of the main mass of the dike, known as the Alice W., but even this minor occurrence was south of a finger of porphyry probably connected with the main dike. The dike extends westerly beyond the limits of the known metallization. It is a curious fact that the swelled portion of the dike parallels the lode. The outcrop of the dike is a conspicuous surface feature of the Lorena claim and to the east and west from this claim. The dike joins the main porphyry mass to the east (see Figs. 1 and 13). Not only is the dike a conspicuous limit of ore but the conditions between the dike and underlying quartzite were unusually favorable to ore deposition. This zone acted as a channel or conduit. The added temperature and pressure within the confined space enabled the ore-forming solutions to penetrate the interior of the rock to an unusual extent.

#### *The Leadville Orebodies and the Dana-Leadville Vein*

The Leadville orebodies, consisting mainly of lead-zinc-silver, but with subordinate copper ore, occurred in the Highland Boy limestone to the northwest of the copper oreshoot. They lay almost entirely on the upper side of the Leadville fault plane; the strike of this "break" is usually N 30° E and the dip about 70° to the east. On the Z level, the vein is faulted by the Occidental Fault and only a small amount of ore occurred above that level.

On the Z level, a band of bedded ore, in limestone, extends easterly from the main "break" for about 200 ft. This ore is low-grade lead-zinc-silver with possibly some copper. Below the level to the sixth floor above the 1300-ft. level, the bedded ore was stoped practically continuously; at the sixth floor, the thickness and grade made mining unprofitable and the shoot apparently died out entirely at about the 1300-ft. level. To the north of the lower portion of the bedded stopes, ore made in and near the Leadville "break" and was continuous with the vein or fissure. This ore extended to the twelfth floor above the 1300-ft. level and had a maximum horizontal extent, parallel to the Leadville, of more than 300 ft. The stopes rarely exceeded 25 ft. in thickness. Below the 1300-ft. level, the ore made to the 1500-ft. and deeper, in two large bodies which were connected by a thin ore band, but the continuous thickness known above the 1300-ft. level was missing.

On the 1400-ft. level, a third oreshoot, of minor importance, came in to the north of the two shoots previously mentioned.

The rocks enclosing the Leadville ore are black limestone and quartzite but predominantly limestone. Below the 1500-ft. level, heavy pyrite occurred persistently in the quartzite.



The Dana-Leadville vein is well developed on the Apex surface on the Chas. A. Dana claim and underground on many of the upper levels. Work near the surface, during the litigation, demonstrated that this vein possessed extralateral rights, but continuity to the Leadville country has never been established. The relation of the known veins led to the selection of the name Dana-Leadville to represent this system. They have been produced by the same general forces and metallized by the same solutions at probably the same time. Actually the veins may overlap, unite upward on the dip, or may be equivalent but displaced by faulting. In

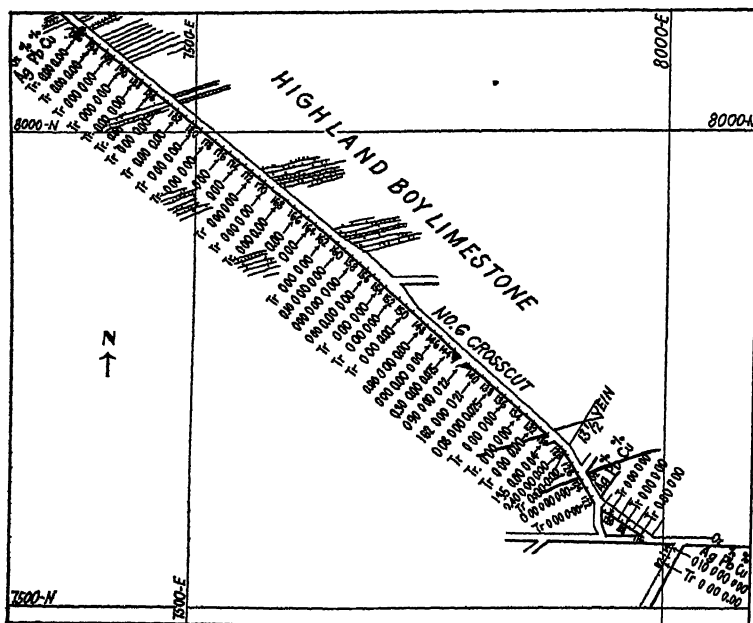


FIG. 6.—UTAH CONSOLIDATED SEVENTH LEVEL.

my opinion, the Leadville vein unites upward with the vein formerly known as the Dana.

### *Ore in Quartzite*

Ore occurred in quartzite in the Oregon stope on the 4C level. This was a portion of the Highland Boy orebody near its upper termination. Ore occurred in the thin quartzite band in the Highland Boy limestone on the 4C level but the first-mentioned occurrence is in the overlying quartzite. The ore extended 20 ft. or more into the overlying quartzite. The rock surrounding the northern portion of the Oregon stope is a heavily metallized quartzite showing unmistakably that the ore removed was similar except as to grade (see Fig. 7).

In the Leadville country, much ore occurred in the quartzite underlying the Highland Boy limestone, particularly on the 1400-ft. and 1500-ft. levels and in the intervening stopes. In 15-5 stope, ore extended horizontally for 40 ft. into the quartzite or for 20 ft. when measured at right angles to the bedding. Numerous specimens, from which thin sections were made, showed the true character of the rock.

The Dana-Leadville vein, on the new Apex 100-ft. level, showed a large body of mill ore clearly in the quartzite. This ore, to the north and east, spread into the beds and occurred predominantly in the quartzite underlying the Parnell limestone. It is a matter of more recent development that the Utah-Apex mill has run largely on quartzitic ore during the last several years.

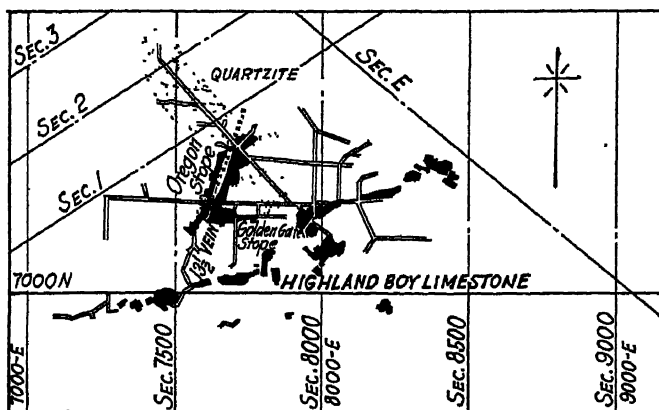


FIG. 7.—UTAH CONSOLIDATED 4-C LEVEL.

From the foregoing examples, it is evident that ore did and does occur in the quartzite in the disputed area. That the orebodies have been predominantly in the limestone is not disputed; but if ore occurs in relatively small amounts in quartzite, it is outside of the claimed limits of a limestone lode.

## MINING GEOLOGY OF OREBODIES IN YAMPA LIMESTONE

### *Succession*

The detailed succession of rocks, from top to bottom, adjacent to the Yampa limestone is as follows:

York-Petro limestone, 1-10 ft.

Quartzite, with at least seven thin included limestone beds, total of 300 ft.

Parnell limestone, 30-50 ft.

Quartzite, 220 ft.

Bullard limestone, 5-20 ft.

Quartzite, with at least one limestone bed about 20 ft. in thickness, total 400 ft.

Yampa limestone, 200-300 ft. grading to quartzite in westernmost exposures

Quartzite, 200-300 ft. including several thin limestone beds near the top.

Some porphyry occurs in the Yampa limestone but, in general, it is conspicuously absent except in the eastern portion. One sill-like occurrence, in the Yampa vein, extends downward from the Consolidated 1300-ft. level; it is also found on various lower levels.

### *Folding and Faulting*

Near the top of the well-known Petro orebodies, the Yampa Limestone suddenly turns from its usual 30° north dip to a vertical dip. The base of the formation, including the Yampa vein, dips quite uniformly at nearly 90° below this turn or fold. The top of the formation is more complexly folded and the entire formation had thickened materially with the usual fracturing and close folding coincident with such thickening.

The sharp bend in the Yampa limestone, starting just below the Apex 1000-ft. level, in the eastern section of the mine, bears a special relation to the fracturing of the limestone and, therefore, to the localization of the orebodies. The quartzites, above and below the Yampa, were relatively competent beds and stood the strain of the bending better than the limestone but nevertheless these beds were also much fractured. The folding produced a series of fissures in the limestone; these were parallel, or approximately so, to the bedding. Conspicuous among them are the Parvenu and Sambo Spur veins. Assuming that at the time of the Yampa Vein metallization there was still a plentiful supply of copper-bearing solutions, a condition which I doubt, the solutions to gain access to the Parvenu and Sambo fissures either had to come in from the east or through transverse fractures from the Yampa vein. The former route appears to have been blocked by the silicated contact metamorphic zone and there were no transverse fissures at this stage of the vein formation; consequently no copper-bearing solutions penetrated the ground in which the Utah-Apex orebodies are now found.

Later the settling of the porphyry produced the transverse fissures, conspicuous among them being the Petro and the Dana-Leadville. These fissures, particularly the Petro, intensified the fissuring and fracturing in the vicinity of the bend and, when the lead-making solutions came through, conditions were favorable and the orebodies were formed. The present condition of fracturing is the sum total of all of the stresses at all times and certainly considerable has occurred since the orebodies were formed. The change from the northwest to the southwest strike introduced a tension in the central segment in addition. The folding ante-

dated the intrusion of the porphyry and there is a reasonable doubt if the intrusion of the porphyry seriously disturbed the beds, as it may have quietly eaten its way by marginal assimilation.

Later faults, without mineralization worthy of special mention, are the Nellie Bly, Major, Andy, and Yampa East. Locally pyrite can be found in all of these faults.

### *Outcrop of Yampa Limestone and Apex of Yampa Vein*

From east to west, the course of the Yampa limestone can best be noted by referring to Fig. 1. It will be seen that the formation extends through the Mercer No. 2 east end line. The outcrop to the west is fairly regular with the apparent variations in thickness due largely to the topography. Near the west central portion of the Yampa claim, a marked variation in petrographic content is to be noted; possibly a thin bed of limestone occurs at the Inland portal but the rock to the north, in the area which should be occupied by normal Yampa limestone, is a calcareous quartzite or a pure quartzite. The explanation is that the limestone beds "feather out" to the west and the wedges of quartzite coming in from the west disappear easterly in a similar manner.

Throughout the central portion of the area, the Yampa vein occurs normally at the base of the Yampa limestone. The outcrop is oxidized and from 2 to 20 ft. of gossan have replaced the original sulfides. One apparent slight dislocation, not observable with certainty at the surface, occurs where the Petro vein cuts the Yampa vein just east of the east end line of the Yampa Extension claim. The Yampa vein throughout the extent of its apex dips north at low angles, usually about 20° to 25°.

Just east of the probable position of the Petro vein, on the Mercer No. 2 claim, occurs the last known exposure of the Yampa vein. On the Treasure claim, but within 100 ft. of the Mercer No. 2 east end line, occur several exposures of a reworked rock which is now a recent conglomerate or alluvium. It is possible that this represents a disintegrated remnant of the Yampa vein lying not necessarily far from the original position of that vein. The position of the apex to the east of the creek is inconclusive, but it may be assumed probable that this crosses the east end line of the Mercer No. 2 claim either at the surface or a short distance underground.

The Yampa vein crosses the south side line of the Yampa claim about 300 ft. east from the southwest corner. This is the projection of the Inland vein as the wash of Sap Gulch covers the apex of the vein. Possibly a "split" from the vein may occur a short distance to the west, as this is the condition on the Inland level not far below the surface. Southerly from the Inland, the vein has a southeast trend due to a combination of flat dip and topography. Possibly the extralateral sweep along the Yampa vein may be limited on the west by a plane passing about 300 ft. east of the west end line of the Yampa claim. With the exception just noted, the extralateral sweeps of the claims, in which the Yampa

vein apexes, pass northerly in such a manner that all the ore mined by the Utah-Apex, in the Yampa limestone, is included within their limits.

### *The Yampa Vein Underground*

Underground, the Yampa vein is a normal fissure vein lying at and near the contact between the Yampa limestone and the underlying quartzite. This contact is one between a competent and a relatively incompetent formation and is necessarily a plane of weakness along which fissuring would tend to localize. Accordingly, breccia and gouge occur and more often they extend into the brittle quartzite below than into the less brittle limestone above the contact. When the solutions carrying copper and iron penetrated the fissure, the conditions of temperature and pressure were such that deposition of the metallic sulfides took place and the Yampa vein was formed. In the ground directly up the dip from the Utah-Apex workings, lead mineralization is really limited to one locality—the extreme west end of the Consolidated 1300-ft. level. A foot of good galena occurred in the lower portion of the Yampa vein; the horizontal extent was about 100 feet.

The various Yampa vein workings, reached from the 7-16 shaft, show that a considerable portion, possibly the major portion, of the ore from these workings was lead ore. From the 4C to the fifth, seventh, T, and Z level, etc. are conspicuous examples of this metallization. It is noteworthy that the overlying limestone is invariably black and that the vein is narrow, probably not exceeding 15 ft. as a maximum thickness. The orebodies are replacements of gouge and breccia and the vein a clear example of a fissure vein.

Separating the various lead orebodies, which were mined from the the 7-16 shaft, are considerable distances where there is no mineralization at the contact. The limestone and the quartzite meet with practically a knife-edge contact and with neither gouge nor breccia. Elsewhere some mineralization took place, usually too narrow or too lean to warrant mining.

On the west end of the Consolidated 4C level, and also between the 4C and the Inland levels, the Yampa vein splits into two portions; one, perhaps both, pass into quartzite which takes the stratigraphic position of limestone farther east.

In the workings of the Utah Consolidated adjacent to the 1300 1500, and 1800-ft. level workings of the Utah-Apex, the Yampa vein differs from elsewhere in that a sill-like porphyry sheet parallels the vein. This is true for more than 1000 ft. on the Consolidated 1600-ft. level and for lesser distances, as developed, elsewhere. Westerly on the 1600-ft. level the vein, including the porphyry sill, lies in the quartzite.

The Yampa case model, Fig. 2, shows that the stoped portion of the Yampa vein is a sheetlike body separate and distinct from the orebodies

occurring in the heavily metallized section near the "bend" in that formation.

## *The Split Vein*

At, or somewhat above, the point where the bedding of the Yampa limestone begins to steepen, a vein "splits" off from the Yampa vein

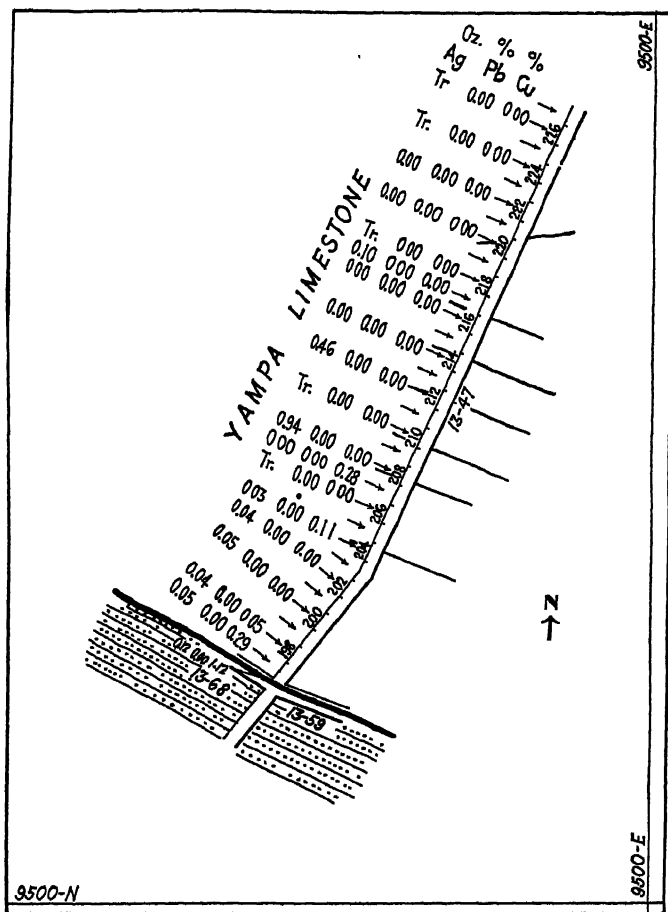


FIG. 8.—UTAH CONSOLIDATED 1300-FT. LEVEL.

and dips northerly at about the angle of the Yampa vein before it assumed the steeper dip of the contact below the fold. The "split" is a fissure vein cutting across the limestone bedding and dipping about 45° northerly. It is seldom more than 8 ft. thick. In going westerly, along the strike, the point of junction with the parent vein drops lower and lower until, at 8560E, the point of junction is at about the 6400-ft. elevation; while at



in the split vein; the galena decreased in quantity with distance from the Petro and less than 50 ft. from the Petro the split again becomes the normal copper vein.

### *The Petro Vein*

The Petro vein strikes northwest-southeast and dips southwest at 50° to 60°. Dips under 50° are known and so are dips greater than 60°.

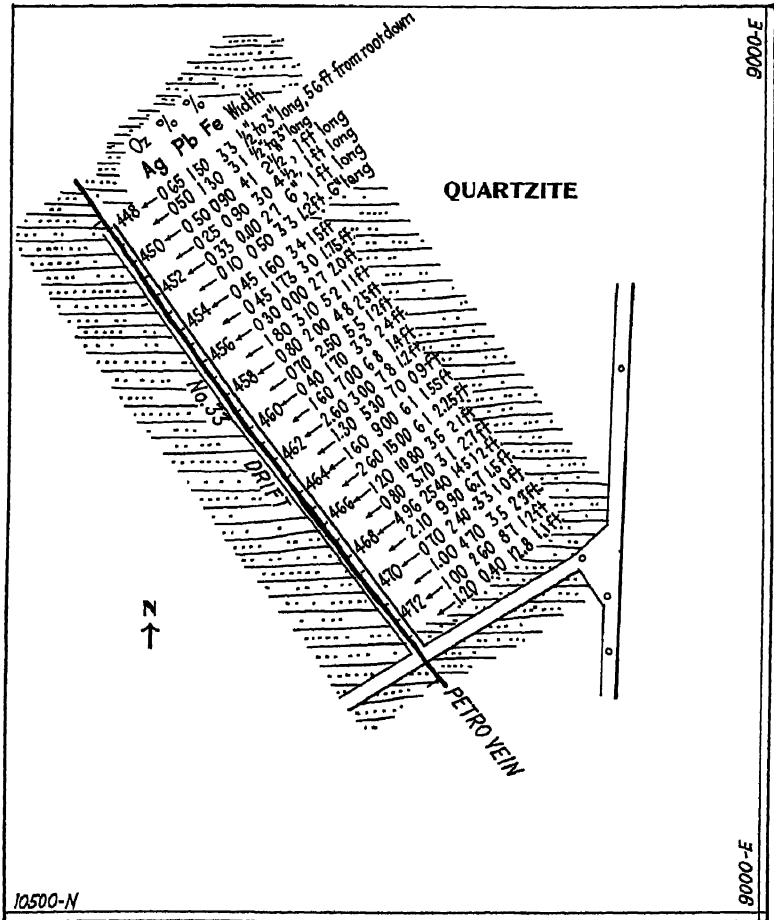


FIG. 10.—UTAH-APEX 700-FT. LEVEL. SAMPLE 448 UP AND DOWN FACE IN FISSURE; REMAINING SAMPLES IN ROOF ACROSS ORE-BEARING PART OF FISSURE.

The Petro is a fault-fissure vein in which the gouge and breccia have largely been replaced by ore minerals. From the Apex 1500-ft. to the 1400-ft. level and above, ore made conspicuously in the vein itself and occurred banded parallel to the strike and dip of the vein. From the 900-ft. Apex level to the 1300-ft., and in some instances below the 1300-ft.,



the normal occurrence is that the metallizing solutions coursed along the fissure and penetrated the easily replaceable limestone near it and was there deposited. It is therefore true that the greater portion of the ore of the Petro vein lies in the limestone, contiguous to the fissure, with attitude approximating that of the limestone bedding. With the exception of the lower portion of 9-stope, Apex 1500-ft. level, and considering the stoping up to the end of 1919, no ore made in quantity at a perpendicular distance from the Petro of more than 150 ft. (see Fig. 9).

The orebodies of the Petro vein, of the lead-zinc-silver type with pyrite, are disconnected pods, lenses or chimneys. They have a decided rake to the southwest.

The Petro vein carries much cupriferous pyrite and galena in the quartzite above the Yampa limestone. In the so-called Lindgren drift, Apex 700-ft. level, the vein is typically developed with the solid sulfide occurring up to several feet in thickness (see Fig. 10).

The Petro outcrops on the surface; it is developed for a vertical distance of more than 2000 ft. and for over 3000 ft. on the dip of the vein.

Two important subsidiary veins are known as the Sambo spur and the Parvenu spur. These spurs strike east-west and dip at steep angles usually northerly. Most of the ore mined by the Utah-Apex from the Yampa limestone has come from the Petro vein and from these two spurs close to the Petro.

#### *Relation of Petro and Yampa Veins*

The mineralization along the Petro vein breaks the continuity of the Yampa vein and is distinctly later. This is particularly well shown on the Craig and 1300-ft. levels. The post-mineral movement along the Petro displaces the Yampa vein and it is not possible to say how much faulting occurred along the Petro before it was metallized; some displacement certainly occurred. The essential thing is that an intersection of veins is conclusively shown. In the raise from the top of 5E stope, 1300-ft. Utah-Apex, the ore made to about 15 ft. vertically below the Petro and the remaining ground below the Petro was only slightly metallized. The Petro is here typically developed and the top of it is a distinct fault plane, with the split vein abutting against this plane. The veins are in close juxtaposition but the occurrence substantiates the other evidence that the veins are intersecting veins. A well-defined fault plane, parallel to the split vein in strike and dip, appears on the north side of the 1400-ft. Apex orebody and continues northerly at its normal dip. This is further evidence that the veins are intersecting veins.

#### *Yampa Limestone Underground*

The metamorphism of the Yampa limestone, which is at a maximum in the eastern workings, nearest the porphyry, decreases and practically

entirely disappears to the west. The occurrence of metallic sulfides also decreases westerly, except that they are most strongly developed just south of the Apex main shaft. The eastern zone shows limestone altered to marble, lime silicate, and ore; westerly, the limestone becomes black in color and comparatively unmetamorphosed.

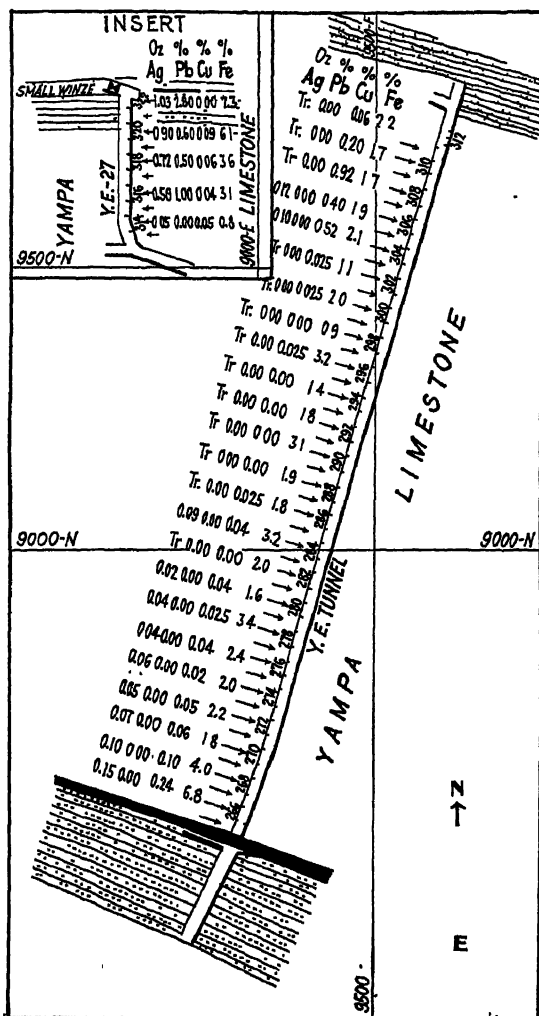


FIG. 11.—Y. E. TUNNEL LEVEL, UTAH CONSOLIDATED MINE.

Reference to the sampling on the Consolidated Y. E. (Fig. 11), and the Consolidated 1300-ft. (Fig. 8), will give the best idea of the general metallization of the Yampa limestone in certain areas.

The stratification is one of the conspicuous features of the Yampa limestone; it is practically always easily seen and the statement, fre-

quently made in connection with limestone-bed litigation, that the bedding has been obliterated by the fissuring and metamorphism, is in no manner applicable to it.

*Metallic Sulfides in the Quartzite above and below the Yampa Limestone*

On the Yampa Extension level, in the overlying quartzite, lead sulfide occurs in considerable quantity (see Fig. 11).

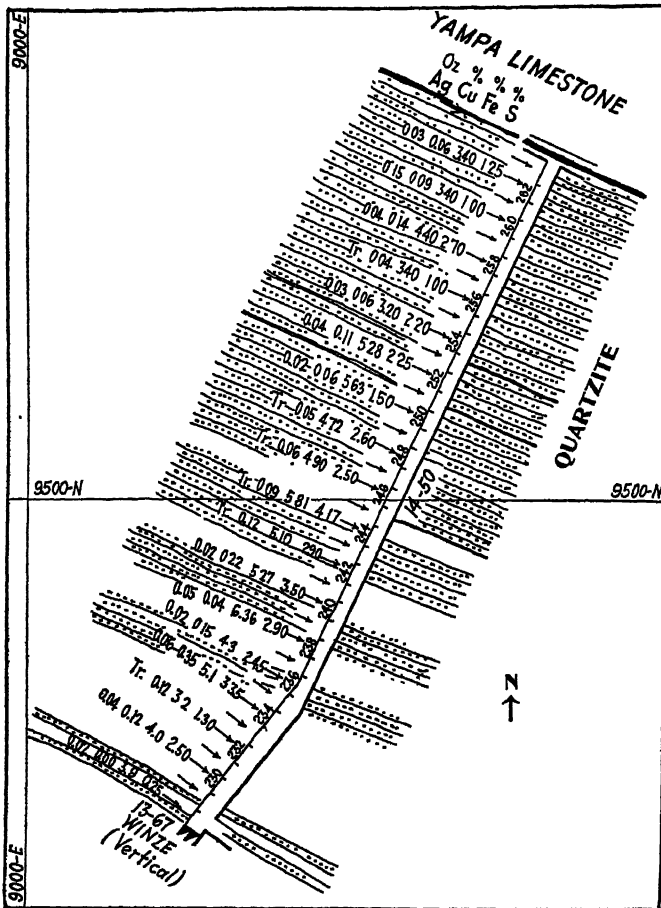


FIG. 12.—UTAH CONSOLIDATED 1400-FT. LEVEL.

On the old Apex 900-ft. level, the top of the oreshoot extended well into the calcareous quartzite lying between the Yampa limestone and the overlying quartzite. The Petro vein, Apex 700-ft. level, carries a continuous band of lead sulfide (see Fig. 10). An orebody, 60 ft. in width, occurred in quartzite on the 4C level, where the Yampa limestone feathers out to the west.

The sub-Yampa quartzite, Consolidated 1400-ft. level, is strongly impregnated with cupriferous pyrite (Fig. 12). An average of about 7 per cent. iron sulfide with about 3 lb. of copper to the ton is carried in this quartzite for nearly 500 ft. in thickness. The total copper and silver in a cube of 1000 ft. runs into startling figures.

From the foregoing examples, it is evident that ore does occur in the quartzite and that the general metallization of this rock is normally equivalent to that of the metamorphosed limestone, away from the orebodies, if it does not actually exceed it.

### *Origin of Veins*

Attention has already been drawn to the fissuring and the fracturing produced during the early folding of the sediments. Some additional fissuring was produced when the porphyry intruded the country rock but the importance of this is not so easily ascertainable as the porphyry could, and doubtless did, to a large extent, eat its way into the sediments by marginal assimilation. If it did not eat its way by marginal assimilation, it seems to me the porphyry came in with a rush and thrust the sediments aside bodily and thus produced an actual displacement of the beds as a whole rather than in smaller units of volume. The settling of the porphyry, subsequent to cooling, produced a set of fissures parallel to the periphery of the mass and these, when later metallized, became the lead veins as we now know them. When these fissures were formed it is probable that the copper metallization was waning and the solutions depleted of that metal and richer in the lead-zinc metals. The latter solutions were essentially lead bearing and the ore was formed in the peripheral veins and to some extent as overlapping waves superimposed on the copper ores. It is, of course, admitted that some lead came out with the first ores, which were essentially copper, but the lead was held longer in solution and carried farther from the source. Similarly, some copper came out with the later lead solutions and we find some copper ore in the Leadville and Petro stopes, particularly the former. With the overlapping of metallization, it is not surprising that some occurrences are obscured. Successive waves of minerals superimposed second and possibly third sets of sulfides on the first set. Several fissures, which cut the Yampa limestone, form small orebodies at the base of that formation, in the country west of the Apex workings, and these orebodies extend but a short distance from the fissures, usually less than 50 ft. When this condition overlaps the copper of the Yampa vein, a situation such as was found in the Consolidated 1300-ft. level, east and west of the Petro, becomes clear and its significance apparent.

The copper ore did not make to the Parvenu zone of the Yampa limestone because there were no transverse fissures to bring the solutions into that territory. It is also possible that the main force of the copper metal-

lization had been spent in the Highland Boy lode since there could not be an unlimited quantity of copper-forming solutions.

The conclusion is obvious that, genetically, there was a difference in the time of deposition, if not an actual slightly different source of the metallizing solutions. By this I do not mean that the lead came from another source than the monzonite but that the greater part of it came from a different center, or came subsequent to the copper, even if it did come from about the same position. The copper came out in the first wave of metallization and penetrated *en masse* the broken up, easily replaceable limestone, nearest the porphyry.

This penetration may to some extent include Spurr's<sup>1</sup> idea of the intrusion of vein dikes very near the porphyry but certainly not at a

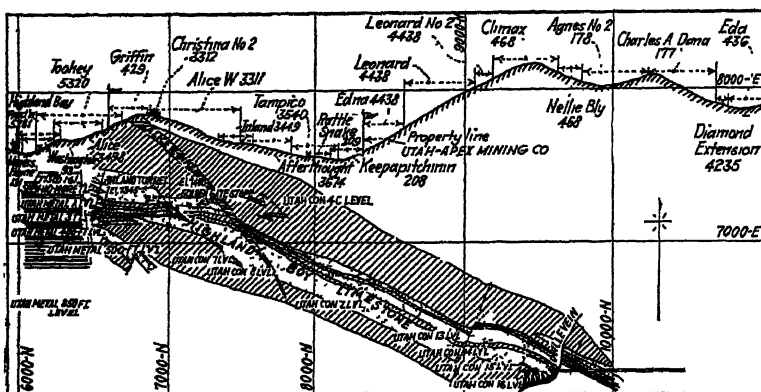


FIG. 13.—TRANSVERSE SECTION "7500" OF HIGHLAND BOY LIMESTONE; COURSE OF N 0° E. ON 7500E, VIEWED FROM EAST.

greater distance. Considerable experience in Mexico leads me to say that Spurr's explanation of the vein dikes is applicable to many of the metalliferous veins, particularly these of Pachuca. The penetration of the metallizing solution, as at Bingham, into a soluble rock, argues strongly for a solution that is highly mobile and, therefore, probably highly aqueous. As a feature that differs slightly from Spurr's conception I thought of many of the Pachuca veins as being formed by a heated ore magma, more or less viscous, flowing into an open fissure filled with water. The resulting mixture was somewhat aqueous even if the ore magma carried little or no water gas.

#### DECISIONS OF TRIAL COURT

The concluding paragraphs of Judge Johnson's decision in the Highland Boy case are as follows:

<sup>1</sup> J. E. Spurr: "The Ore Magmas." McGraw-Hill Book Co. New York, N. Y., 1923.

In the case at bar we cannot say that the whole of the Highland Boy limestone has been profoundly broken, altered and mineralized, and has thereby obtained an individuality which, apart from other differences, clearly distinguishes it from the neighboring rock.

On the contrary, in this case we have a large body of limestone lying between the two orebodies, comparatively unbroken, unaltered, and unmineralized.

In this case we cannot say, as was found by the court in the Lawson case, that the orebodies are not separated, one from another, by any defined boundaries.

On the contrary, in this case the orebodies are separated by the inclosing porphyry sheet and fingers and by the barren, unmineralized, and comparatively unbroken and unaltered limestone.

It has not been shown by extensive exploration or actual mining in the Highland Boy limestone that the mineralization has been so general that its only defined limits are the quartzite walls which bound the limestone, or that within it one may reasonably expect to encounter ore by driving or crosscutting in any direction, as was found by the court in the Lawson case. There has been only a limited exploration and no actual mining in the great mass of limestone lying between the two orebodies in the Highland Boy limestone. This limited exploration shows no mineralization above, and but slight mineralization below. If this condition of the limestone continues throughout its mass, the miner would not encounter ore by driving or crosscutting in any part of it, whatever his expectations might be.

The contention of the defendants in the Lawson case, stated in finding numbered 5 above, has no parallel in the contention of the plaintiff in this action.

It cannot be said in this case that the ores of the Leadville orebody lose their identity, or that they cannot be distinguished from the orebodies found in the Highland Boy limestone above, as was found by the court in the Lawson case to be the condition with respect to ores claimed by the defendants to belong to the Ashland fissure.

It was conceded in the Lawson case that there were no walls separating the cross-fissures from the bodies of ore in the limestone.

In this case it is insisted with great earnestness that the porphyry sheet and fingers and intervening limestone constitute a definite, certain, and well-defined boundary separating the two orebodies.

On the other hand, in the Lawson case many of the facts are the same as, or similar to, the facts in this case. The orebodies which were the subject of litigation in the Lawson case were located only a few thousand feet from the orebodies which are the subject of litigation in this case. The Jordan limestone and the Highland Boy Limestone are parts of the same sedimentary bed, and each lies between the same underlying and overlying quartzite. The sedimentary beds were subjected to the same forces by which they were uplifted and more or less tilted and bent as we now find them. In both, the sedimentary beds have been more or less broken and penetrated by masses of porphyry ascending from the deep. In both, the predominating minerals are copper and lead, found mainly in the limestone, deposited there by replacement from solutions coming up from the masses of porphyry beneath. In the Lawson case the court found the whole of the Jordan limestone to constitute one broad lode. In this case it is admitted that the upper segment of the Highland Boy limestone constitutes one broad lode. In both the Jordan and the Highland Boy limestones and the quartzite and other limestone beds lying above, are found numerous faults and fissures, some of them, as the Ashland in the Jordan and the Leadville in the Highland Boy, containing mineral. Except as heretofore noted, in both the limestone is similarly broken, altered and mineralized.

The expert witnesses called by the defendant gave it as their opinion that the Highland Boy limestone intervening between the upper orebodies and the Leadville ore-

body may be prospected by the miner with reasonable expectation of finding ore by crosscutting in any direction. It is the opinion of these witnesses that the Highland Boy limestone is one broad lode.

The expert witnesses for the plaintiff gave it as their opinion that the upper orebody below and south of the intruded sheet and fingers of porphyry is a broad lode, and that these porphyry intrusions constitute its northern boundary. It is the opinion of these witnesses that the Leadville orebody is a distinct entity, and that the intervening limestone is unmineralized and barren and constitutes no part of either the upper lode or the Leadville orebody.

The experts called by the respective parties and who have testified in this case are men of great learning as geologists and of wide experience as mining engineers. I do not question the sincerity of any one of them. The opinion of each group commands attention and respectful consideration. So evenly are they balanced in learning and in experience that it would be difficult to determine on which side is the greater weight of the evidence, if it was not for the existence of an undisputed fact in the case confirming the opinion of the expert witnesses called by the plaintiff.

The witnesses for the defendant testified that this intervening limestone was ground in which the miner might reasonably expect to encounter ore by driving or crosscutting in any direction. As stated by counsel of the defendant in their brief, for more than twenty years this property has been operated by the defendant and its predecessors, during which time there has been taken from the mine ore of the approximate value of forty million dollars. Notwithstanding such immense resources, the defendant has failed, except to the limited extent heretofore indicated, to prospect this limestone or develop it.

I cannot escape the conviction that if there was reasonable expectation of finding ore by driving or crosscutting in any direction in this limestone, the defendant, as a practical miner, at the time it ran tunnels and drifts through this intervening limestone, or since, would have crosscut the limestone, and that it would have extended some of the many short drifts and crosscuts now terminating along the upper and lower edges of this undeveloped country.

The barren limestone lying between the upper lode and the Leadville orebody breaks the continuity of the lode, and the question of the exact identity of wall or boundary is unimportant. "In the existence of such body and to the extent of it," as stated by Judge Hallett in the *Cheesman* case, 116 U. S. 586, language approved by the Supreme Court of the United States, "boundaries are implied."

I am of opinion that the broad lode apexing within the mining claims of the defendant does not include within it the intervening barren limestone or the Leadville ore body. Judgment will be entered for the plaintiff.

Judge Johnson's decision in the Yampa case is as follows:

The question for determination in the cases now under consideration is the ownership of certain orebodies found mainly in the limestone bed called the Yampa limestone. The Utah Consolidated Mining Co., the plaintiff, claims that the Yampa limestone is a broad lode and that the orebodies in dispute, found in the Yampa limestone beneath the surface of the mining property of the defendant, belong to and are the property of the plaintiff by virtue of the extralateral rights conferred by the laws of the United States in such cases.

The defendant denies that the Yampa limestone is a broad lode and claims the ownership of the disputed orebodies on two grounds:

First.—Because it is the owner of the mining claims within which the disputed ores are found; and

Second.—Because, as it asserts, the disputed ores are found within a vein whose apex is within the boundaries of mining claims owned by it, and that it is the owner of the orebodies claimed by the plaintiff by virtue of the extralateral rights conferred by the laws of the United States.

These suits were brought by the plaintiff to enjoin the further removal of ores from said Yampa limestone by the defendant, and to secure an accounting for the value of the ores already removed.

The Yampa limestone has been mined and developed by the plaintiff and its predecessors along its dip a distance approximately of 3000 ft., and along its strike about one mile.

There is a marked difference in the appearance of the orebodies found in the Yampa limestone and in the appearance of the orebodies found in the Highland Boy limestone, as is clearly shown by the maps and models introduced in evidence in the Highland Boy case and in these cases. The maps and models show in the Highland Boy limestone an immense deposit of ore made up of a great number of closely associated and related orebodies, extending from the quartzite below to the quartzite above, from 200 to 1000 ft. in width, and raking along the dip of the limestone in a northeasterly direction a distance of approximately 3000 ft. The maps and models show in the Yampa limestone to the south the orebodies developed by the plaintiff and its predecessors; to the north the orebodies developed by the defendant and its predecessors. The orebodies developed by the plaintiff and its predecessors consist of a flat sheet of ore whose apex is shown on the models extending a distance of approximately 2500 ft. within the boundaries of the mining claims of the plaintiff. This flat sheet of ore divides into two branches as it descends beneath the surface along the dip, one branch extending towards the northwest, the other towards the northeast and in the direction of the orebodies developed by the defendant and in dispute in these actions. In the neighborhood of the disputed orebodies the flat sheet turns over and becomes nearly vertical. It has an average thickness of 5 or 6 ft. and lies mainly between the quartzite below and the Yampa limestone above. In the easterly part of the mine this ore is copper ore; in the westerly part of the mine, lead ore.

Commencing near the surface and a short distance below the outcrop of the Yampa limestone, and extending in a northeasterly direction for a distance of approximately 1000 ft., there are a number of lead stopes in the limestone above the thin, flat sheet of copper ore described above; and beginning at the easterly end of the lead stopes just mentioned there are a group of copper stopes in the limestone above the thin, flat sheet of copper ore, running almost east and west, a distance of 700 or 800 ft.

Except the group of lead and copper stopes in the limestone above the flat sheet of ore above described, there are no orebodies or mineralization not clearly associated with the flat sheet of ore, until the orebodies in dispute are reached below.

The limestone above and overlying this thin, flat sheet of ore—in the country intervening between the orebodies in dispute and the local occurrences of lead and copper ore in the body of the limestone near the surface, a distance along the dip of about 1800 ft., and east and west along the strike a distance of about one mile—is, except to a very limited extent, undeveloped and unprospected, and, so far as known, is practically unmineralized, unchanged, unbroken limestone.

Considered alone and apart from its environment I do not think it would be seriously disputed that the thin, flat sheet of ore and mineralization lying between the limestone and quartzite is a fissure vein of which the quartzite is the foot wall and the limestone the hanging wall; and the question for determination is whether, when considered in relation to its environment this thin, flat sheet of ore is itself a vein, or whether it is only a broad shoot of ore deposited along the base of the limestone, which, in connection with the lead and copper stopes in the limestone near the surface and the large bodies of lead ore in dispute in these actions, and other considerations found to exist, gives character to and constitutes the Yampa limestone a broad lode.



It is the contention of the plaintiff and the opinion of its expert witnesses that, taking into consideration every factor that should be considered in reaching a conclusion, the thin, flat sheet is only an ore shoot, and that the Yampa limestone is a broad lode.

It is the contention of the defendant and of its expert witnesses that, taking into consideration every factor that should be considered in reaching a conclusion, the thin, flat sheet of ore and mineralization is a fissure vein with the quartzite as a foot wall and the Yampa limestone as a hanging wall, and that the Yampa limestone is not a broad lode.

In these cases, as in the Highland Boy case, the burden of proof rests upon the Utah Consolidated Mining Co., and the same considerations which determined the final conclusion in the Highland Boy case are applicable and controlling in these cases. I am constrained to hold that the plaintiff has not by a preponderance of the evidence sustained its contention that the Yampa limestone is a broad lode, and I am of opinion that the thin, flat sheet of ore lying between the quartzite below and the limestone above is the vein which outcrops within the boundaries of the mining claims of the plaintiff, and the vein which gives to the plaintiff extralateral rights beneath the surface of the mining claims of the defendant. The orebodies in dispute are no part of this vein.

As this conclusion disposes of these cases, it is unnecessary to decide whether or not the orebodies mined by the defendant beneath the surface of its mining claims are within or a part of the Petro fissure and subsidiary fissures, and at this time I expressly refrain from doing so.

Judgments will be entered for the defendant.

### DECISIONS OF CIRCUIT COURT OF APPEALS

The decision of the Circuit Court of Appeals, Eighth District, in the Highland Boy case stated its opinion in language similar to that used by the trial court and affirmed the decision of that court.

In the Yampa case the decision of the circuit court is as follows:

In considering the Yampa footwall vein as it relates to the mineralization of the Yampa limestone we are of the opinion that it shows too much; that is its extent and location tends to show that it is the vein or lode which gives to appellant its extralateral rights, and thereby negatives to a certain extent the claim that the Yampa limestone is a broad lode.

It remains to consider the question as to whether the orebodies in dispute are a part of the Yampa foot-wall vein. Of course, if the claim of appellant that the Yampa limestone was a broad lode had been sustained, the question now to be considered would be immaterial, or, if it had been decided that the orebodies in question were a part of the Yampa foot-wall vein, the question of a broad lode would be immaterial, but appellant has the right to maintain its title to the orebodies in dispute by urging alternative sources of title, although in sustaining one it abandons the other. Before taking up the question to be considered certain criticisms made by counsel for appellant as to the decree entered below may be noticed. There was and is only one major issue presented by the pleadings for decision. That question was and is whether appellant is the owner of the orebodies in dispute. Appellee asked for no affirmative relief. It is satisfied with the decree. The decree decided that appellant was not the owner of the orebodies in question through either of its claimed sources of title. This met the issue presented by the pleadings. No further decision was necessary or proper. The testimony in regard to the orebodies in question was relevant for two reasons: (1) For the purpose of showing that said bodies were or were not a part

of the Yampa foot-wall vein; (2) as tending to show the source of the mineralization of the Yampa limestone. It is claimed by appellant that appellee came in contact with the orebodies in dispute prior to 1909, by driving what is called in the evidence the Parvenu tunnel, and shown upon appellee's 1000-ft. level maps; that this tunnel was a crosscut about 2000 ft. in length chiefly in quartzite and entering beneath the surface on the west side of Carr fork, and so pointed that, if the Yampa limestone continued its northerly dip of 30°, the tunnel would have intercepted the downward extension of the foot wall of the Yampa limestone. At the time of the driving of this tunnel, however, the steepening of the dip of the Yampa Limestone had not been developed, so that the tunnel, instead of penetrating the limestone at the foot wall, barely entered the hanging-wall margin of the limestone. That some 18 months later appellee, having exhausted the ore in the upper limestone lodes (Parnell and York Petro) began operations in the Yampa limestone, and from these stopes appellee has mined a large amount of ore. Appellant, gradually developing its mine and extending its workings downward upon orebodies on the dip of the Yampa limestone, or, as appellee would say, along the dip of the Yampa foot-wall vein, reached the area entered by appellee, and, as appellant claims, made connections in ore with the workings of appellee. Appellant further claims that the orebodies removed by appellee were not discovered nor developed by following downward upon any ore or from the surface, but through crosscuts driven in a southerly direction from the Parvenu tunnel, which at that point was 1000 ft. underground, and which had not been driven along any ore whatever. Admitting, however, all that is claimed as to the manner in which the appellee discovered the orebodies in dispute, we do not see how these facts have any bearing upon the question at issue. Appellee's motive or the manner in which it proceeded has no relevancy in determining whether the orebodies in dispute are a part of the Yampa foot-wall vein. As we have stated, however, the claim of appellant, we briefly state that appellee claims that the Parvenu tunnel was run entirely beneath the surface of its territory, that the Petro, Louisa, Dana, and Leonard fissures extended from the surface down for a considerable distance at the time of the running of the tunnel and were already well known, and that the tunnel was run not only for the purpose of making a connection with the bottom of one of appellee's shafts or inclines, and as a main channel for getting ore out of its mine, but also with the idea of intersecting these fissures in depth. We omit however any further discussion of this matter as immaterial.

Appellant claims that the orebodies in dispute are a part of the Yampa foot-wall vein for the reason that the evidence shows a junction or union of branches or split veins, as they are called in the record, extending from the Yampa foot-wall veins to and coming in contact with the orebodies or some of them. It is admitted by appellee that one of the branches or split veins comes down to the No. 5 orebody or to be more specific to the fissure extending up from it where the vein is intersected and cut off, but counsel contend, and we think correctly, that an admission that there is an intersection is not equivalent to an admission that there was a union or connection. We are of the opinion that the evidence shows that at the only place where the Yampa foot-wall vein comes in contact with any of the orebodies in dispute such contact constitutes an intersection and not a junction or union. As has been said before, appellee admits that appellant is the owner of such spurs and split veins which are a part of the Yampa foot-wall vein.

All the witnesses for appellee testify that these spurs or veins pinch out or die in a comparatively short distance from the parent vein. Appellee mined the orebodies in controversy for eight years before this litigation was commenced, and for six years before that time appellant knew that appellee claimed the orebodies in dispute and was engaged in mining them. There is abundant evidence to sustain a finding by the court that the orebodies in dispute are closely associated with a fissure and its branches or

spurs which extends from the surface downward into the Yampa limestone and not mineralogically connected with the vein underlying the limestone bed. This fissure was for several years before the commencement of this litigation known in Bingham as the Petro. It is so called in the evidence by appellee. In the evidence of appellant it is called the Smith fault or fissure. We must assume that the trial court found, judging from what it expressly found, that the orebodies in dispute had their origin in the Petro fissure. *Silver King Coalition Mines Co. v. Conkling Mining Co.* (April 11, 1921) 256 U. S. 18, 41 Sup. Ct. 426, 65 L. Ed. This fissure comes down through the limestone nearly at right angles to the Yampa foot-wall vein and intersects the limestone beds. Its total width is 7 to 8 ft. We are satisfied from the evidence that the Petro is the ore carrying channel which mineralized the Sambo or Parvenu orebodies, which are two separate ore zones related to the Petro fissure. What has been said in regard to the effect of the finding of the trial court upon the question of a broad lode apply also to its finding that the orebodies in dispute were not a part of the Yampa foot-wall vein. As late as *Silver King M. Co. v. Conkling M. Co.* *supra*, the Supreme Court said:

"But the experienced District Judge, after careful consideration, was of the opinion that the ore belonged to the vein. We see nothing to convince us that he was wrong."

The burden of proof to sustain both contentions of appellant namely, that the Yampa limestone was a broad lode, and that the orebodies in dispute were a part of the Yampa foot-wall vein, was upon the appellant. We agree with the trial court that the burden was not met. We have not found it possible in an opinion of reasonable length to analyze the evidence of the experts who have testified in the case. They all have their opinions and theories, but the miner determines what a lode is largely from physical facts.

We have carefully considered the evidence, and are not convinced that the trial court was wrong upon either issue passed upon by him.

The decree below, being in our opinion right, is affirmed.

#### ACKNOWLEDGMENTS

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■

## Rôle of Secondary Enrichment in Genesis of Butte Chalcocite\*

[*Secondary Enrichment Investigation Contribution No. 15*]

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(New York Meeting, February, 1924)

IN 1900, when the public first heard of "secondary enrichment," the Butte chalcocite seemed clearly supergene. Mining, through successive regions of leached capping, bonanza sulfide, and sulfide less rich, had paused at lean bottom levels which, though chalcocite-bearing, suggested the waning of copper. The deepest chalcocite, at 1500 ft., was yet too shallow to disturb the supergene hypothesis. But, with deeper mining, lean levels yielded to fat ones. Here and there they showed, within the same vein, an inverted distribution, chalcopyrite above and chalcocite below. To the miners' astonishment, they carried chalcocite, unaffected by cross faults, on an independent course to the depth of 2500 ft. The pattern of ore distribution, hitherto revealed only in fragments, was now appearing in perspective, and, in the depth of the chalcocite, was beginning to make Butte differ from all districts where the chalcocite is indubitably supergene. The idea of hypogene origin at length came into favor; by 1913, when Sales<sup>1</sup> advocated this origin, the argument had become a powerful one.

This argument rested on field evidence; but, already, there was beginning to emerge microscopic evidence not included in this argument. Especially pertinent was the proof that (1) the deep chalcocite lies in-mixed with bornite, often microscopic; (2) the deep chalcocite often replaces bornite; and (3) replacement of bornite by chalcocite is accomplished more easily than that of pyrite, enargite, or chalcopyrite. The microscopic evidence has been accumulating for ten years and it demands

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\* A paper presented at a joint meeting of the American Institute of Mining and Metallurgical Engineers and the Society of Economic Geologists.

<sup>1</sup> Reno H. Sales: Ore Deposits at Butte, Mont. *Trans.* (1913) 46, 3-109.

a review, in its turn, of the hypogene hypothesis. Such a review, fitting the new facts into the broader field structure, is the purpose of this paper.

### FIELD ARGUMENT

The commercial study in Butte has provided an impressive compilation of fact and inference. It has reduced the wilderness of veins to orderly record; despite the emphasis on faulting, it has allowed no hypothesis suggested by field observation to escape, and no hypothesis, not showing sturdy qualities against repeated field attack, to survive. The chief source of field information on Butte is, obviously, this study.

The presumption favors the hypothesis of supergene origin. For, in districts other than Butte, an overwhelming proportion of the chalcocite is supergene. And, in Butte, within a zone 100 to 1200 ft. thick just below the leached capping, there occur bonanza replacements of pyrite, enargite, and bornite by chalcocite, in all respects resembling the conventional supergene enrichments of these other districts. On the broad argument from analogy, all the chalcocite seems supergene.

The broad argument, however, makes merely a starting point for discussion. That discussion must involve such characteristics as descent of chalcocite to unusual depths, which give to Butte a look of strangeness. It must involve, on the other hand, the exceptional abundance of deep-seated bornite there and its ease of replaceability by chalcocite. Furthermore, it must question whether or not the deep-channel conditions provided by the veins may promote deep enrichment, and whether or not the bornite itself is hypogene.

### *Intermixture of Chalcocite with Other Sulfides*

Sales<sup>2</sup> gives the following evidence as suggestive of hypogene origin.

The intimate association of chalcocite with bornite, pyrite, and enargite in such a manner that all must be regarded as having been deposited at the same time and under similar conditions.

With the hypogene origin, the intermixture of chalcocite with other sulfides is, indeed, compatible. But it is quite as compatible with the hypothesis that the chalcocite has replaced a member of a sulfide mixture. The field observation, that the chalcocite is so involved as to seem contemporaneous, must yield to the microscopic observations that, when bornite is absent, deep chalcocite is absent, and that deep chalcocite often replaces bornite. Much chalcocite is, then, proved younger than the other sulfides and the argument of association is transferred from chalcocite to bornite or to any other sulfide which it might be proved to replace.

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<sup>2</sup>*Op. cit.*, 94.

*Apparent Replacement of Rock by Chalcocite*

Sales<sup>3</sup> says:

Chalcocite directly replaces altered granite at deep levels. The power of cold meteoric waters to effect direct replacement of granite in quantity is seriously questioned by the writer.

So far as the field evidence goes, the chalcocite may be wholly a replacement of bornite, for the veinlets of chalcocite threading the granite are proved by the microscope to carry at least a little bornite.

*Paucity of Deep Enrichment of Pyrite*

The enrichment of pyrite in Sales' "sooty chalcocite zone"<sup>4</sup> diminishes downward somewhat suddenly. Below that zone, although steely chalcocite is abundant, an occasional tarnish, and a rare, heavier coating of chalcocite or covellite in vuggy openings, are the sole enrichment of pyrite.

In all the deep workings, the pyrite, with these insignificant exceptions, is uncoated, and this means that the bulk of the pyrite has undergone not even the beginnings of enrichment. Often, pyrite is "corroded" by some other sulfide, but the corrosion is of a sort not known to be supergene; and, nearby, bright, striated crystals project into open spaces and into masses of bornite and chalcocite.

This is a strange condition, if the steely chalcocite be thought supergene. For other districts testify that when bornite is half changed to chalcocite, some pyrite in the vicinity shows always a tarnish and often a coating. A hand specimen of pyrite, and even a ton, might stay clean; but scarcely a whole great region of deep enrichment. In Butte, the supergene hypothesis involves, then, an hypothesis of contrast in replaceability between pyrite and the replaced sulfide greater than that known in other districts to exist between pyrite and bornite. But the field evidence fails to prove that the replaced mineral is bornite. This passes the matter on to the microscope.

*Downward Decrease of Kaolin*

The term kaolin, as here used, includes not only kaolinite, but also the kaolin-like materials such as halloysite.

The kaolin pertinent to the argument is, of course, that of pre-mine origin. Hot, moist workings of whatever depth, especially in rock having pyrite and fresh feldspar, develop kaolin 2 ft. inward from the exposed faces. The recognition of such kaolin is readily made in deep cuttings with the pick.

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<sup>3</sup> *Op. cit.*, 95.

<sup>4</sup> Sales' "sooty chalcocite zone" is the zone of indubitable supergene enrichment and is characterized by chalcocite and covellite, sooty and in firm coatings on pyrite, in addition to the steely chalcocite usual in deeper levels.

The pre-mine kaolin is chiefly a replacement of feldspar and sericite and is a close associate of the chalcocite or covellite replacing pyrite. In Sales' "sooty chalcocite zone," it is common. Below that zone, it is scarce and closely associated with the incipient enrichment of pyrite. In a large way, the kaolinization and the enrichment of pyrite go together.

We may waive the consideration that the kaolin wanes downward because of a change to unfavorable rock. For no such change, as, for example, a decrease in feldspar or pyrite, occurs with depth. But does this mean that the deep chalcocite, unaccompanied by kaolin, is therefore hypogene?

Absence of kaolin does not strictly prove absence of enrichment where bornite is the replaced mineral. For, under certain conditions, solutions capable of chalcocitizing bornite may be impotent to kaolinize feldspar. Absence of kaolin, nevertheless, does suggest absence of important enrichment. In other districts having undoubted supergene enrichment of bornite, and having rock appropriate for kaolinization, both kaolinization and enrichment of pyrite are present all through the enrichment zone. On the basis of experience, the expectable condition is only a little chalcocite here and there replacing bornite without making kaolin. The actual condition in Butte is deep chalcocite, abundant and widespread through the deepest copper-sulfide mines in the world, and essentially free from kaolin in all but the upper levels.

#### *Downward Persistence of Chalcocite*

While a whole bottom level may suggest loss of chalcocite, subsequent, deeper levels recover it. Observers of the district say that, compared with other copper-bearing sulfides, chalcocite, at 3000 and at 1000 ft. below the surface, is equally abundant.

This means, according to the supergene hypothesis, an unexampled depth of enrichment and it demands explanation. A proposed explanation postulates a former deep water table. Thus, the Continental Fault relatively depressed the Butte district 1500 ft.; the Flat, near Butte, has its bed rock 1000 ft. below the surface of the mines of medium elevation and buried at one place 600 ft. deep. Brown's Gulch, 6 miles south, has its bed rock at least a little further below these same mines, and buried at least a little deeper.

That, on these accounts, the water table was formerly deeper than at present in relation to the orebodies is, of course, possible. But if it was, and if it has risen since enrichment and oxidation, it has so risen as now to coincide with the bottom of oxidation.<sup>5</sup> This, an accidental result, is improbable.

The argument of coincidence between water table and bottom of oxidation is specific. It implies a water table not deeper in past times

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<sup>5</sup> Sales: *Op. cit.*, 44.

than at present. The physiographic argument, on the other hand, is vague. It fails to assist in the decision.<sup>6</sup>

This matter of the downward persistence of chalcocite will be further considered under other headings.

*Age Relation between Chalcocite and Certain Veins and Faults*

Sales<sup>7</sup> says:

. . . the Rarus fault sharply cuts all the important ore veins, displacing them hundreds of feet, so that in the intersected veins the possibility of surface waters effecting an enrichment of the truncated portion of the veins lying beneath the fault is extremely remote. The upper displaced segment of the O'Neill vein, for example, is no richer in chalcocite than the subfault segment, excepting within the chalcocitization zone directly beneath the oxidized zone. . . . The moving waters did not enrich the fault, as it carries no ore, neither did these solutions spread out to other veins cut by the fault. The altered condition of the crushed zone of the Rarus fault, the presence of much disseminated pyrite and quartz together with the fact that a later fault (Middle) cuts and displaces the Rarus fissures, tend to show that geologically the Rarus is not a recent fissure; therefore, the water circulation responsible for the chalcocite older than the Rarus fault must be far removed from the meteoric groundwaters of today.

The relations between the Rarus Fault and the veins are such that enriching solutions descending a vein would have to turn, follow the fault several hundred feet, and turn again into the vein. This is assuming the fault to be old. It must be old, at least in part, for it localizes pyrite. But may it not be old only in part? And may not the separation result largely from another, post-enrichment part? This is conceivable. But the Middle Fault, displacing the Rarus about 50 ft. and later than the latest Rarus movement, is sufficiently old to show no scarp. The probabilities favor enough pre-enrichment movement to separate well the intersected veins. Let us, then, assume such movement.

That descending solutions might actually find their way from the vein segments above to segments below seems possible. And, because of the easy replaceability of bornite, an important mineral of these veins, they might enrich below the fault the veins they had enriched above, ignoring the fault because it carries pyrite as its sole sulfide.

This is possible, but is it in any degree probable? In the first place, it requires a complicated chain of favorable conditions, with the chances, on general principles, against it. But, again, in no other district has chalcocite of proved supergene origin been found to jump a gap of the sort here described. But it may be argued, with some show of reason, that no other district has exactly this structural situation or has veins altogether so favorable to enrichment; no other district has such an abun-

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<sup>6</sup> W. W. Atwood: Physiographic Conditions at Butte, Mont., and Bingham Canyon, Utah. *Econ. Geol.* (1916) 11, 697-740.

<sup>7</sup> *Op. cit.*, 95.



dance of hypogene bornite and, at the same time, such well-defined easy channels to carry the water to great depth.

This counter argument as to the channel conditions is unsound, for, as will be shown later, some of the veins that carry deep chalcocite are especially poor water carriers. But, as to the especial favorability to enrichment, it is worthy of sharp scrutiny. Grant to Butte ore an ease of replaceability beyond that elsewhere known; and grant an ensuing replacement that could ignore the wonted barriers; and these very effects, astonishing though they may be, might follow.

This is the only escape, not only from this Rarus Fault argument as proof of hypogene origin for the chalcocite, but also from the argument of deep chalcocite and from others to come later. It is a subject for fine critical methods and on it the microscopic study is especially focussed. Its consideration will be undertaken later in the paper.

#### *Occurrence of Chalcocite Bodies with No Apparent Superior Source*

This argument is concerned chiefly with the so-called Blue veins or Fault veins. These dip steeply, dislocate the veins of the Anaconda system, and carry abundant gouge and important but discontinuous orebodies.

Following is a quotation from Sales<sup>8</sup> in reference to this argument:

. . . many of the largest and most important rich chalcocite-enargite oreshoots in these veins do not extend upward to within 500 to 800 ft. of the surface. Not only do the copper minerals fail, but the common gangue minerals, quartz and pyrite, drop out, so that the oreshoots are capped by hundreds of feet of barren crushed granite and fault clay marking the plane of movement. In two instances, notably in the Jessie and Blue veins, oreshoots reach the surface, but in these cases the upper 500 ft. of the shoots differ materially in mineralogical composition from the richer ores at greater depths.

Following is another quotation from Sales:<sup>9</sup>

In the Jessie vein . . . the oreshoots have been opened by continuous workings from the surface to the 2200-ft. level . . . Within a vertical distance of from 50 to 75 ft., there is almost a complete transitional change (downward) from chalcopyrite ore to an ore consisting of chalcocite, bornite, enargite, pyrite, and quartz, with only small amounts of chalcopyrite. This character of mineralization has continued to the deepest levels yet opened. . . .

It is impossible to conceive of a surface water origin for the chalcocite lying below the chalcopyrite capping. There certainly is no apparent adequate source for the copper. Where the chalcopyrite ore suffers oxidation, the larger part of the copper is held in the oxidized zone as an oxide or carbonate, and, even assuming that a part of the copper was carried downward, it is quite impossible for the writer to believe that it could have remained in solution while passing downward over the chalcopyrite-pyrite ore, to be later deposited as chalcocite from 800 to 2200 ft. below the surface.

So far as this vein is concerned, we cannot eliminate the possibility, in the eroded country above the present surface, of oreshoots that liberated

copper to make the deep chalcocite. But why the extraordinary descent of the copper-bearing solutions through depths of 500 to 800 ft. of chalcopyrite before they achieve their enrichment? Why, even in the first foot below the capping, the merely incipient change of chalcopyrite to chalcocite?

In the other veins, there is a similar possibility that oreshoots existed in the eroded country above the present surface. But certain veins, as was shown on p. 938, though chalcocite-rich below, are tight at the top, and shut off from a possible upper source.

But could not all these veins have received copper from tributary channels intersecting them at or above the present top of the chalcocite? Such channels are wholly hypothetical. None have been found, although the development and stoping of the ore leaves them few places in which to hide. Furthermore, in other districts, supergene chalcocite has not been proved to get its enriching copper through other than the simple channels of the upper, oxidized part of the ore deposit.

There might, however, be a longitudinal migration of copper-bearing solution along the vein. But the orebodies are often insulated along the vein by fault clay—so insulated that enrichment by the passage of water is unlikely. Nevertheless, the downward migration of solutions through the impervious vein, their leaving the chalcopyrite clean at the top of the vein, their making emphatic enrichment below, their access in tributary channels, or their migration laterally along even an impervious vein—these might still occur on a single condition, that of easy replaceability already mentioned and later to be discussed.

#### *Failure of Chalcocite to Depend on Vein Intersections or Vein-fault Intersections*

The following is from Sales:<sup>10</sup>

The oreshoots are not connected or related in any manner with cross-fissuring or later faulting . . . the Blue vein oreshoots do not occur at the intersections with older quartz-pyrite veins, but on the contrary, curiously enough, they are almost universally found in the intervals between the important older veins. . . . No apparent relation exists between the Blue-vein shoots and the later Steward faults; in fact, repeated observations of such intersections show, beyond question, that the oreshoots were in existence prior to the appearance of the Steward faults.

On an hypothesis of supergene origin, this independence of intersections indicates a fundamental difference of process from that known in other districts; for in other districts the enrichment, instead of ignoring such intersections, is controlled by them. Here, again, the only way out is the postulated easy replaceability mentioned above.

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<sup>10</sup> *Op. cit.*, 97.

*Failure of Chalcocite to Favor Pervious in Contrast with Impervious Veins*

The estimation of perviousness in the Butte veins is made by three methods: (1) The comparison in physical character between this vein stuff and that of other districts; (2) the comparison between one Butte vein and another in the depth of oxidation and of sooty chalcocite; and (3) the comparison between one Butte vein and another in the amount of water yielded in mine workings.

In many districts there is a kind of vein stuff known to be highly pervious. This is typified by the Bingham disseminated ore. It carries tiny stringers of quartz, sulfides, sericite, and sometimes adularia, so abundant that scarcely a hand specimen lacks them. It carries these minerals soaked through the interstringer fragments of altered rock. It is brittle, rather than tough, and, when broken artificially, flies into blocks and fines. The high perviousness of this material is caused by tiny quartz-lined vugs, post-ore fractures, and contacts between the fine-grained alteration minerals. Kaolin is seldom sufficiently abundant to stop the openings.

Proof of great perviousness consists in oxidation over many acres to depths of several hundred feet. The perviousness is so uniform as to permit oxidation down to a sharply defined level; it is so great as to permit oxidation to keep pace with erosion and to descend close to the water table; it is so great, furthermore, as to permit pervasive enrichment to strike downward far into the sulfides. Even the more persistent cracks may fail to dominate in the distribution of supergene copper.

Such material is more pervious than all others likely to be near it. Fresh porphyry or gouge or garnet may bear sulfide exposed to daylight, alongside a deeply leached capping of such material. The disseminated ore itself makes a medium for water travel, and its draining in one place by a shaft drains the body away from the shaft. A barrel of water poured out on the surface would pursue a rapid and almost vertical journey to the water table.

In the Butte veins are large quantities of material resembling that described. This material, however, is coarser grained; it has larger vugs and must be regarded as more pervious. Because, however, of differences in its continuity and because of differences in the amount and quality of the wall-rock alteration, the veins, from the standpoint of perviousness, constitute two sharply contrasted groups.

Those of the Anaconda system, except where interrupted by faults, are continuously pervious as far as they are known on strike and dip. The Blue veins, on the other hand, though in ore rather similar, have that ore in shoots isolated both on strike and dip by regions that are gouge-filled and unquestionably, by comparison, impervious. While 1 cu. ft. of

water was traversing 1 sq. ft. of Blue-vein section, 100 or 1000 cu. ft. might traverse an equal Anaconda-vein section. On the basis, then, of general information, there is indicated a marked contrast in perviousness between the Anaconda veins and those of the Blue system. There is indicated, furthermore, a similar contrast between the central part of the district, with its widespread granite alteration, and the outside part, with its granite alteration thinly bordering the veins. Is this contrast evidenced in the depth of oxidation? The depth of oxidation varies extremely from place to place and vein to vein. Sales<sup>11</sup> says:

The depth of the zone of oxidation in a particular locality is largely dependent on the character of the veins and the enclosing country rock, to a greater extent, in fact, than on the topographic features. The deepest oxidation is found in the great zones of altered granite . . . where it runs from 100 to 400 ft. wide, averaging in the neighborhood of 250 ft. Under similar conditions of granite alteration, the heavily mineralized veins of the Anaconda system show deeper oxidation than the fault veins . . . In regions unaffected by the widespread hydrothermal processes . . . the depth of oxidation along the veins of the Anaconda system averages about 75 ft., and that of the fault veins 20 ft., with frequent variations in both classes of veins,

The depth of "sooty chalcocite" (see footnote 4) varies somewhat similarly from place to place and vein to vein. Sales<sup>12</sup> says:

Sooty chalcocite . . . is confined particularly to those portions of the veins lying immediately below the zone of oxidation . . . The veins of the Anaconda system, or the quartz-pyrite series, are deeply oxidized as a rule, and in these veins the sooty chalcocite reaches its greatest development. In the fault veins, the zone of oxidation is usually of but slight vertical extent, and since the primary ores seldom extend upward to the surface, the development of sooty chalcocite is of but little importance.

Regarding water, Sales<sup>13</sup> says:

In the early days of Butte mining the water level was encountered in the shafts in the region of the contact between the oxidized and sulfide ores. This was true, however, only in areas of altered granite or where the opening was made within a vein. A shaft sunk in the normal unaltered granite between faults and veins, perchance missing a water course, might extend to great depths as a dry shaft. On the other hand, a shaft put down in the altered granite areas became a wet shaft as soon as the general water level was reached, whether a vein was encountered or not, the whole mass of the altered rock being practically saturated.

It has been repeatedly observed that the well-developed fault fissures do not serve as the most important channels for the movement of the present day ground-waters. . . . Of much greater importance as water carriers are the veins of the Anaconda system, fissures, cracks, and shear zones of relatively slight displacement. The Anaconda veins are frequently of a porous nature and contain many cavities, vugs, and water courses. They are especially good water carriers where cracked or broken by later fault movements. The orebearing faults of the Blue and Steward systems are alternately wet and dry along the strike . . . Frequently the oreshoots contain no water, and it is probable that they have been dry ever since the close of the period of thermal water activity, when the ores were deposited.

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<sup>11</sup> *Op. cit.*, 40.

<sup>12</sup> *Op. cit.*, 49.

<sup>13</sup> *Op. cit.*, 44.

These contrasts in perviousness bear vitally on the question of supergene enrichment. Ought not the Anaconda veins, more pervious than those of the Blue and Steward systems, and ought not the middle of the district, more pervious than the outside, to show more of such enrichment? Actually, neither the Anaconda veins nor the middle of the district shows a higher chalcocite ratio. In the pervious region, that ratio is about the same as elsewhere.

Control of the deep chalcocite by superior perviousness, a marked characteristic of chalcocite known to be supergene, is here absent. That it is absent, suggests that the deep chalcocite is not supergene, and it constitutes the most important field argument for hypogene origin. From this argument, the only obvious escape is the hypothesis of easy replaceability already mentioned and later to be discussed.

### *Position Attained by Field Argument*

The hypothesis of supergene deep chalcocite in Butte carries implications strange to experience. It demands enrichment, deep and thorough, leaving feldspar unclouded and pyrite untarnished; and enrichment so penetrating that usual controls are ignored. Gouges, holding water stagnant, lack influence, though they cut and block a vein down which enriching water may cascade. The several parts of a vein, contrasted in the possession or lack of intersecting veins, and in the alternation of vuggy quartz with obstacles of gouge; and the several veins themselves, contrasted in the continuity or interruption of their pervious materials: these are enriched to the same degree. The 3000-ft. level shows the same enrichment as the 1000-foot.

The mere strangeness of these implications, however, fails to prove the supergene hypothesis absurd. It compels a search for some Butte peculiarity to match this one and explain it. Does not Butte, in some conditions other than enrichment, so differ from all other districts that the rules of experience will not here apply? Some such conditions may still remain unimagined. But, of the hypotheses at hand, only one survives field argument. That is the hypothesis of easy replaceability, and this hypothesis makes the principal theme for the remaining discussion. We are, therefore, reduced to a dilemma: Either the deep chalcocite has replaced some mineral or minerals of unusually easy replaceability, or that chalcocite, by present opinion, is hypogene.

### MICROSCOPIC ARGUMENT

#### *Reliability of Samples*

It remains for us to examine the microscopic argument, and especially that on the subject of easy replaceability and the nature of the replaced sulfide. For the use of such an argument, proof is needed that



FIG. 1.—COARSE, OBVIOUSLY PLEOCHROIC COVELLITE CUT BY CHALCOCITE; MOUNTAIN VIEW SOUTH VEIN, 900-FT. LEVEL.  $\times 290$ .



*Photographed by J. Murdoch.*

FIG. 2.—FINE COVELLITE VEINLETS CROSSING BORNITE BUT HALTING AT CHALCOPYRITE; JESSIE VEIN, APEX DRIFT.  $\times 65$ .



FIG. 3.—BLUE AND WHITE CHALCOCITE LATTICE. MOUNTAIN VIEW SOUTH VEIN, 600-FT. LEVEL.  $\times 100$ .

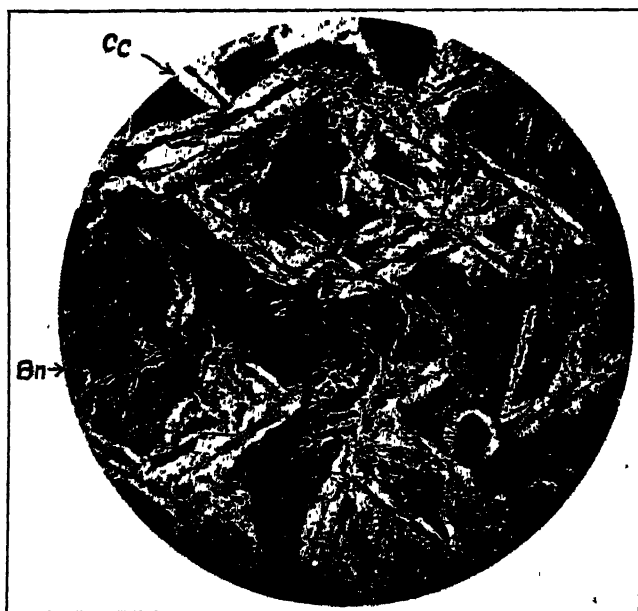
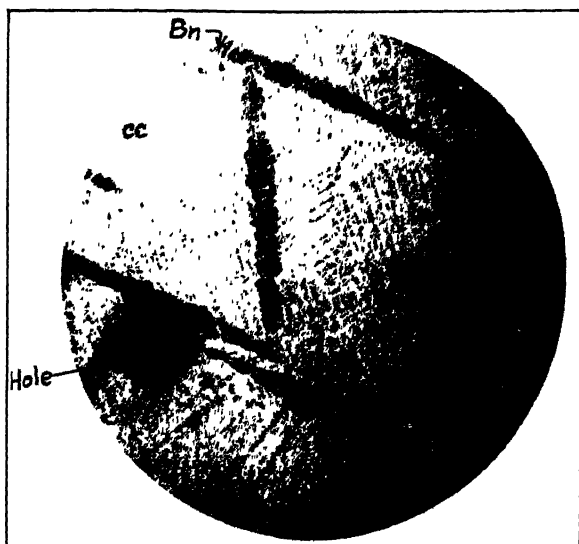
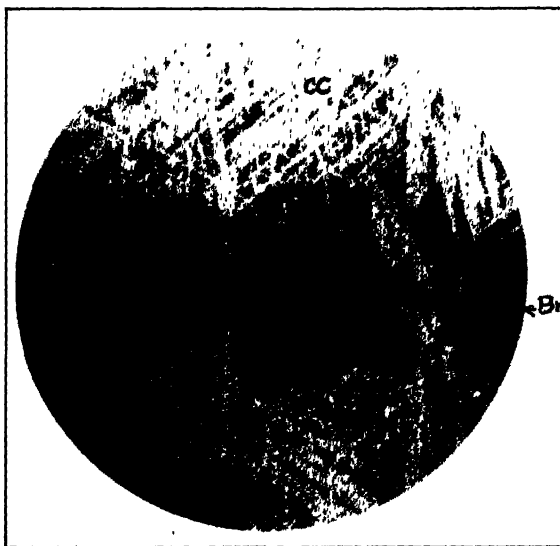


FIG. 4.—BORNITE-CHALCOCITE LATTICE WITH BORNITE CLEAVAGE CONTROLLING CHALCOCITE AND WITH MEDIAL VEINLETS OF LIMONITE; SHANNON VEIN, 1400-FT. LEVEL.  $\times 100$ .



*Photographed by J. Murdoch.*

FIG. 5.—BLUE AND WHITE CHALCOCITE LATTICE CARRYING BORNITE SPLINES, THE BORDERS OF WHICH ARE INVADDED BY THE WHITE CHALCOCITE LAMELLAE; THERE IS NO CONCORDANCE IN ORIENTATION BETWEEN THE SPLINES AND THE LAMELLAE OF THE LATTICE; THE SPLINES MAY BELONG TO SKELETAL CRYSTALS; LEONARD MINE.  $\times 65$ .



*Photographed by J. Murdoch.*

FIG. 6.—SAME AS FIG. 5.  $\times 375$



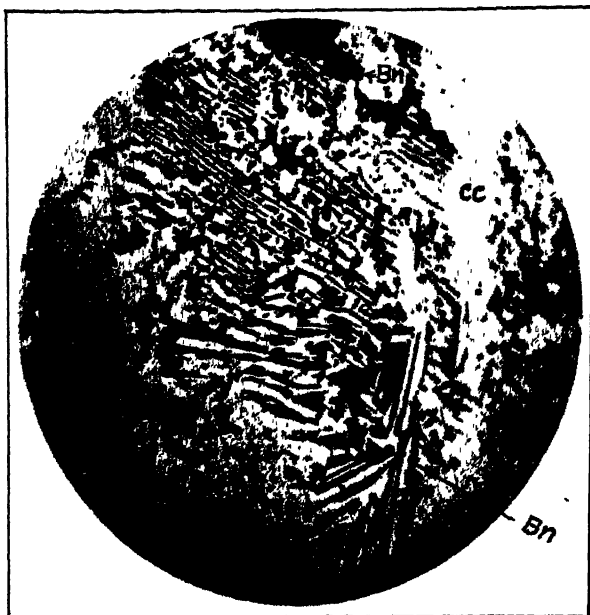


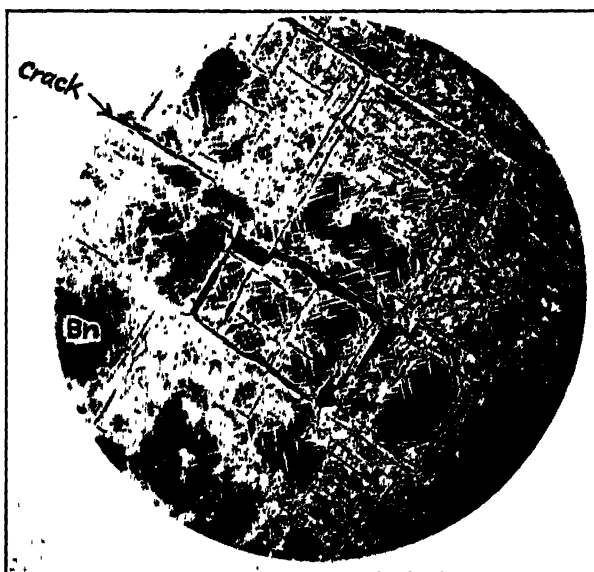
FIG. 7.—BORNITE-CHALCOCITE GRAPHIC STRUCTURE WITH TENDENCY TOWARD LATTICE STRUCTURE; SHANNON VEIN, 1400-FT. LEVEL.  $\times 290$ .



FIG. 8.—BORNITE-CHALCOCITE GRAPHIC STRUCTURE; SNOWBALL VEIN, 2200-FT. LEVEL.  $\times 100$ .

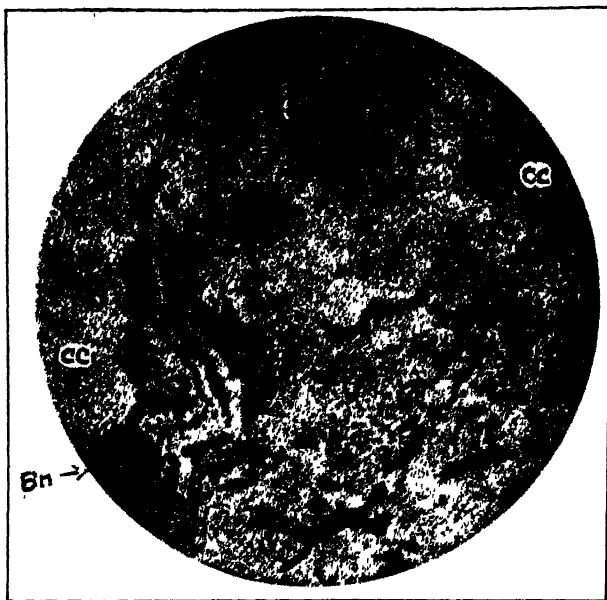


FIG. 9.—INCIPIENT LATTICE OF CHALCOPYRITE INVADING BORNITE ALONG CLEAVAGE CRACKS; LEONARD MINE, 1500-FT. LEVEL.  $\times 290$ .



*Photographed by J. Murdoch*

FIG. 10.—BORNITE-CHALCOPYRITE LATTICE WITH BORNITE CLEAVAGE CONTROLLING CHALCOPYRITE; GAGNON MINE, 2200-FT. LEVEL.  $\times 65$ .



*Photographed by J. Murdoch.*

FIG. 11.—BORNITE-CHALCOCITE IN IMPERFECT GRAPHIC WITH PARALLELISM OF ALIGNMENT.  $\times 65$ .



FIG. 12.—PATCHY CHALCOCITE IN BORNITE; STEWARD MINE, 3700-FT. LEVEL.  $\times 100$

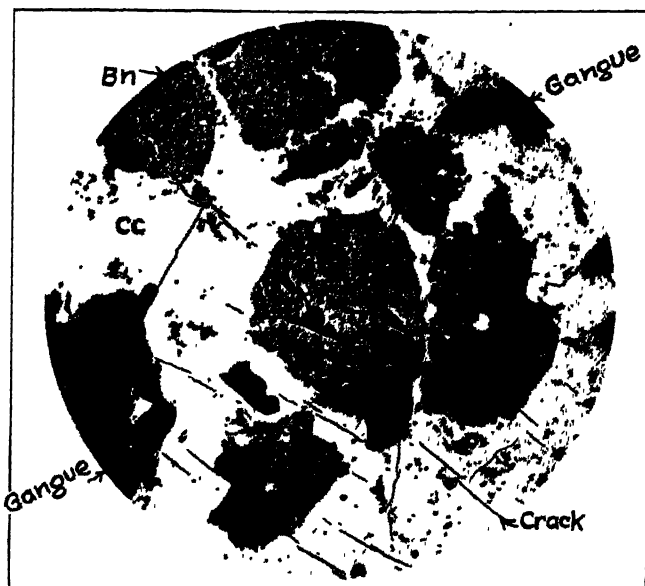


FIG. 13.—BORNITE-CHALCOCITE IN MUTUAL BOUNDARY STRUCTURE WITH EMBAYMENTS OF CHALCOCITE SUGGESTING REPLACEMENT OF BORNITE; THE BORNITE HAS A "FUZZY" BOUNDARY; ELM ORLU MINE, 1500-FT. LEVEL.  $\times 50$ .

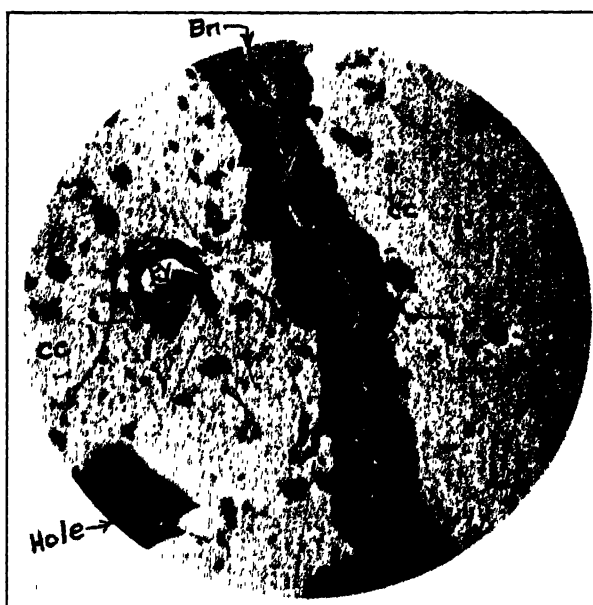


FIG. 14.—BORNITE FOLLOWING A CRACK IN CHALCOCITE, BUT HAVING MUTUAL BOUNDARIES; SUBGRAPHIC BORNITE BLEBS IN CHALCOCITE; SNOWBALL VEIN, 2200-FT. LEVEL.  $\times 100$ .

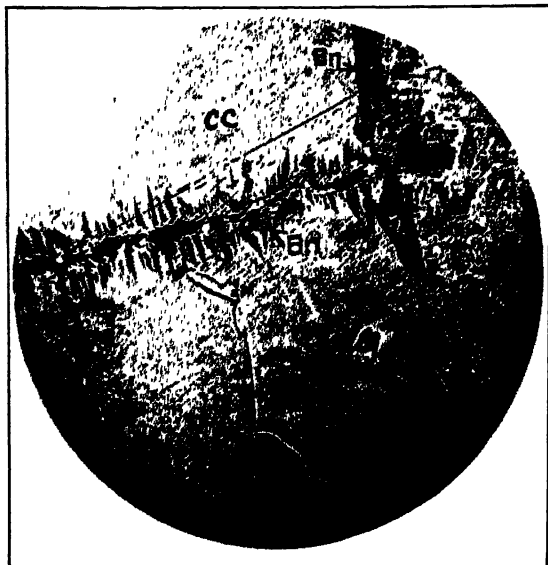


FIG. 15.—BORNITE WITH SHAPES OF POINTED FLAMES BORDERING LIMONITE VEINLET IN CHALCOCITE AND SUGGESTING REPLACEMENT OF CHALCOCITE: BORNITE-CHALCOCITE LATTICE.

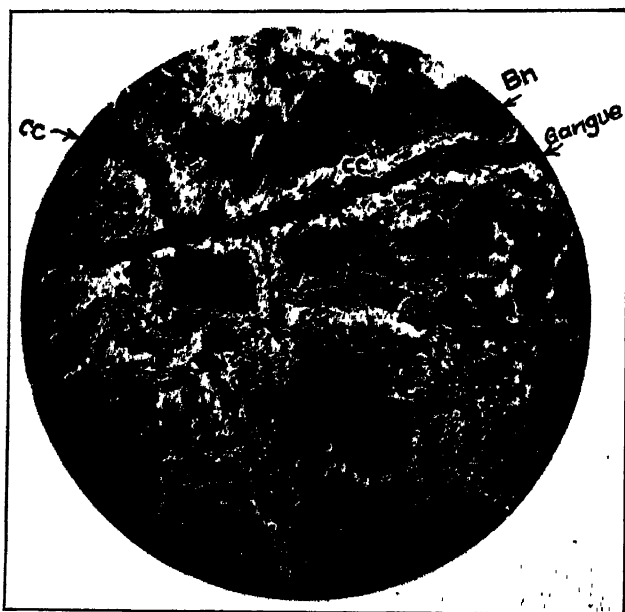


FIG. 16.—CHALCOCITE FOLLOWING GANGUE VEINLETS IN BORNITE; MOUNTAIN VIEW SOUTH VEIN, 400-FT. LEVEL.  $\times 100$ .

the specimens make a fair sample. A fair sample of the copper in the Butte veins would consist of specimens by the tens of thousands. With the one thousand specimens, then, studied by us, not through and through, as by assay, but only on surfaces, could we hope to gain a comprehensive view?

The copper content rises to 15 per cent. and falls to 1 per cent. within a foot of vein length. But the microstructures, fortunately, vary to no such degree. They comprise about a dozen principal varieties. Five hundred specimens of rich copper ore from the central mines include all these varieties within them. Another five hundred from the

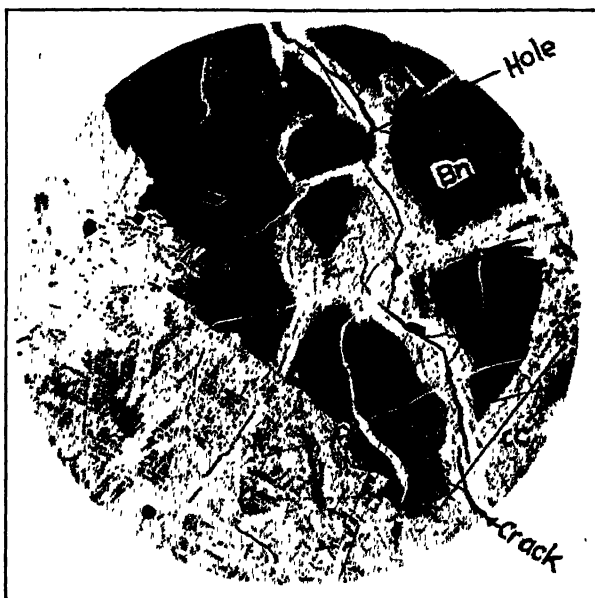


FIG. 17.—BORNITE-CHALCOCITE LATTICE AND CLEAR BORNITE CUT BY CHALCOCITE IN CRACKS; MOUNTAIN VIEW SOUTH VEIN, 400-FT. LEVEL.  $\times 100$ .

same region, studied in a few microscopic fields, such as appear in photomicrographs, yield discordant conclusions, but studied over whole polished surfaces, comprising from five hundred to ten thousand microscopic fields, they yield nothing significantly new. Moreover, the one thousand specimens studied by us are corroborated by about the same number studied by others, and by hundreds from other districts, showing structures simpler but similar to those in Butte.

The microscopic work, combined with field observation, has yielded results having not only a qualitative but also a quantitative aspect. Thus, field evidence shows that chalcocite, with here and there a little bornite, undergoes no notable relative decrease with depth. The microscope shows this chalcocite, except in the vein tops, to carry bornite so univer-

sally as to establish a high degree of probability that a square centimeter surface of chalcocite lacking bornite would be hard to find. It establishes, in a quantitative way, a proportionality between macroscopic chalcocite and microscopic bornite.

### *Covellite*

Though covellite has but a meager and occasional development in Butte, its possible use as an index of supergene origin requires discussion.

There are three contrasted varieties of covellite in Butte. The first occurs at all depths, is coarsely crystalline, and makes plates as large as 10 cm. across. The euhedral outlines of the plates, their great size, their failure to contain remnants of unreplaced sulfides, their enclosure of pyrite and bornite between adjacent buckled plates, and their partial replacement by chalcopyrite and by chalcocite (Fig. 1), suggest this covellite not to be a replacement of an older sulfide. Much of it, being idiomorphic, suggests growth in open spaces or in non-confining matrix. There is nothing in its structures typically supergene.<sup>14</sup> Yet its size and idiomorphism cannot be accepted as proof that it is hypogene. Any consideration of covellite as a criterion of origin must include the fact that covellite, like pyrite and quartz, tends to assume its own crystal form, and might do so and grow into open spaces, or soft matrix, or older sulfide, even in supergene processes. Some well and coarsely crystallized covellite is probably hypogene and some may be supergene.

The second variety of covellite is very fine grained. It replaces bornite in rosettes, and in veinlets generally following small cracks in bornite and boundaries between bornite and other minerals (Fig. 2). This variety is observable principally in the microscope and the total amount is small in comparison with the first variety. It diminishes rapidly with depth and has not been found in the deeper workings; it is unquestionably supergene. It is diagnostic of supergene replacement; its cessation downward indicates a diminution of such replacement, but its absence is no proof that such replacement by chalcocite has not occurred, for supergene chalcocite is far more widespread than supergene covellite and the two tend to be mutually exclusive.

The third variety of covellite exists in the friable, actually sooty, fine-grained mixture of covellite with chalcocite characteristic of the upper levels. Its formation may, in some cases, have been accompanied by an increase in porosity and by a positive decrease in copper. It is diagnostic of supergene alteration.

### *Hypogene vs. Supergene Origin for the Bornite*

Proof of supergene origin for the bornite would carry with it proof of similar origin for the chalcocite. Can the bornite, by any chance, be

<sup>14</sup> L. C. Graton and J. Murdoch: Sulphide Ores of Copper. *Trans.* (1913) **45**, 26.

proved supergene? The outstanding facts suggested by the microscope are that: A large part of the bornite (or, rather, of the composite bornite-chalcocite) is either an open-space filling or a replacement of quartz, sericite, or feldspar; perhaps a tenth is a replacement of enargite and pyrite; a tenth is intergrown with enargite; a modicum is a replacement of tennantite and tetrahedrite; and another modicum is a replacement of sphalerite. In a half dozen specimens, bornite may replace chalcocite (Figs. 14 and 15).

Mixtures of bornite and pyrite are commonly designated as the result of "corrosion." The pyrite is clearly older and replaced; it lies as clusters and groups of rounded masses in a clear expanse of bornite; or as solitary masses far removed from the others (Fig. 2). Rarely, it is cut by well-defined veinlets or swaths of bornite. But marked angularity of the remnants and their obvious control by cracks and grain boundaries, processes characteristic of the supergene replacement of pyrite by chalcocite, especially in its earlier stages, are here absent.

Mixtures of bornite and enargite likewise show rounded boundaries. The enargite is invaded by extremely numerous and irregular tongues of bornite (with chalcocite) and these tongues are distinctly thinner than the bodies of enargite between them. The cleavage of the enargite, in the typical occurrence, exerts no influence on the distribution of the bornite.

In addition to the replacement structures, the bornite has structures that suggest contemporaneity with the enargite. These structures are the simpler varieties of the so-called intergrowths, especially the "mutual boundary" in which each mineral lies within the other in lobes and cusps. There is an absence of the more intricate intergrowths, such as graphics, characteristic between bornite and chalcocite. And in all the bornite-enargite structures, not only those suggesting contemporaneity but also those of replacement, there is a curious predominance of one mineral over the other; the specimen is either bornite-chalcocite with minor enargite, or enargite with minor bornite-chalcocite.

The bornite supposedly filling open spaces or replacing rock stuff occupies irregular veinlets sometimes bounded by crusts of quartz and pyrite, or vugs, or angular openings in quartz. There is here no suggestion of its replacement of any other sulfide. For, though, in the same polished surface, pyrite and enargite abound in other open spaces, in these particular areas the bornite is free from other sulfides except chalcocite. Or, if pyrite and enargite are present, they often have such relations as to suggest strongly their existence as a prebornite lining in the vug and their burial at length under the bornite; pyrite cubes not infrequently lie covered or enclosed by bornite. The origin of a part of the bornite in open spaces may be considered highly probable.

If some of the bornite is open-space filling or replacement of rock, and some of it is an intergrowth with enargite, is the bornite not therefore



proved hypogene? Within the microscopic field, the mutual structure actually grades into the replacement structure; and, on the other hand, it grades into the open-space structure. The relations indicate essential contemporaneity, and hypogene origin for all the bornite.

Another argument for hypogene origin consists in the contrast between these structures and those of supergene chalcocite. Supergene chalcocite follows obvious channels of admission, such as cracks and grain boundaries, and leaves remnants depending, in size, on the number of the traversing channels and the degree of replacement effected through these channels. Nothing is better established than that the replacement can go to any stage whatever. But the remnants of pyrite and enargite in the bornite-chalcocite bear rounded rather than angular outlines; and the replacement proceeds, not by creeping along the channels of easy access, but by flooding the mineral field and leaving tiny residuals scattered far and wide. These differences suggest differences of origin.

But, we need not depend on these microscopic details alone. Supergene bornite in other districts is scarce, which fact makes improbable such quantities of supergene bornite as would be postulated by the supergene hypothesis in Butte. Moreover, all the arguments of large-scale distribution for deep hypogene chalcocite apply to bornite, and with increased force. The bornite, if supergene, must replace pyrite or enargite, minerals yielding slowly, and must do this under conditions unfavorable to enrichment. The bornite is hypogene.

#### *Replacement of Bornite by Chalcocite*

The types of bornite-chalcocite microstructures are:

*Type 1.*—The chalcocite is controlled by gangue and sulfide boundaries, and by fractures in the bornite (Figs. 16 and 17). Structurally, it is a replacement not distinguishable from that by supergene chalcocite in pyrite and enargite, for the chalcocite occupies the same inter-remnant channels, and the bornite remnants are similarly angular and dependent in number, size, and disposition on the number, width, and arrangement of the invading channels. The chalcocite veinlets often possess a dark medial crack, empty or filled with limonite, copper pitch or an unknown mineral; this crack is the channel of replacement from which the chalcocite widens out on either side against the bornite, and its limonite presumably results from oxidation by cupric sulfate.<sup>15</sup> The chalcocite border may be either clear or hazy. Where it is hazy, lower magnifications show a transition zone usually bluish. This type is characteristic of undoubted supergene replacement and occasional but not characteristic in deep chalcocite.

<sup>15</sup> E. G. Zies, E. T. Allen, and H. E. Merwin: Some Reactions Involved in Secondary Enrichment. *Econ. Geol.* (1916) 11, 407-503.

*Type 2.*—This type is often a companion of and grading into Type 1. The chalcocite is controlled by cleavage directions in the bornite and makes with the bornite the so-called lattice structure. Of the lattice structure, there are two kinds, the first of which is the type discussed. Here, from the main channels, chalcocite penetrates for some distance sidewise into the bornite in sharp gashes or blades, forming a regular, diamond-shaped pattern along the borders. The directions taken by the blades are shown, by etching the bornite, to coincide with the bornite cleavage. A frequent companion of this structure is one in which microscopic (supergene) chalcopyrite in similar gashes or blades follows the bornite cleavages just ahead of the chalcocite. This type is characteristic of undoubted supergene replacement and is moderately abundant in deep chalcocite.

*Type 3.*—Type 3 is the second variety of lattice structure. The characteristic distinguishing this lattice from that of Type 2 is its independence of visible channels (Fig. 3). Areas covering a quarter of the microscopic field, and wholly detached from major lines of control, adjoin areas of clear bornite or chalcocite. Some times the lattice pattern is so minute and the chalcocite replacement has gone so far that, under low magnification, merely lines of pinkish blur mark the presence of the bornite residuals in the chalcocite; higher magnification shows the bornite to survive only in tiny diamonds. The replacement of the bornite by the chalcocite is a matter of doubt. The two minerals might be contemporaneous. In some instances, the chalcocite might be the older. The structure is not produced by undoubted supergene replacement.

*Type 4.*—The bornite has an appearance suggesting its sudden breaking down throughout its length and breadth with no reference to cleavage or other obvious lines of control. The bornite area carries irregular gashes and branching areas of chalcocite with tattered edges, so uniformly distributed and so small that, under low magnification, it appears as bornite somewhat off color. The structure is not produced by undoubted supergene replacement.

*Type 5.*—This type has the "mutual boundary" structure. This is similar to the structure existing between bornite and enargite; lobes and bulbs of the bornite penetrate the chalcocite with the same frequency and in the identical manner in which similar shapes of the chalcocite penetrate the bornite (see Fig. 12). The structure "looks no more in one direction than in the other" and were the chalcocite and bornite to change places, the significance of their relations would be unchanged. Neither obviously replaces the other. But, grading out from this structure, often within the limits of a single polished surface and sometimes within the limits of a single microscopic field, are structures showing clear replacement of bornite by chalcocite—lattices, veinlets and obviously invading bulky areas with rounded residuals. The chalcocite of these replacement

structures is continuous with that of the other: it is identical in color and is often proved to be of identical crystallographic orientation. The chalcocite of the two structures seems little different in age. The mutual boundary structure occurs at all depths and is not produced by undoubted supergene replacement.

*Type 6.*—The graphic intergrowth. This has long been well known; its resemblance to eutectic structure and the consequent argument that the chalcocite and bornite are of contemporaneous origin, has made it conspicuous. It shows the mutual boundary, complicated and smaller in scale; it is the mutual boundary with sharper curves. Occasionally, it is so coarse as to be seen without the microscope; often it is so fine as to require high magnification. The two minerals occur in intimate intermixtures. In one part of the field they may be characterized by the mutual structure; in another, by a graphic representation of the two minerals disposed in hooks, dots, lobes, and stringers (see Figs. 7, 8, and 11); and this may yield abruptly to an area of clear chalcocite or bornite. Or, the graphic form may grade into the lattice. "Emulsions" of bornite in chalcocite are not uncommon; and these, like the plainly graphic structures, may lie adjacent to areas of clear chalcocite or bornite. Often, within a given polished surface or microscopic field, the graphic form grades into structures that mean replacement. But these, like those grading from areas showing the mutual boundary, are of a kind strange to supergene enrichment. The graphic structure occurs at all depths and is not produced by undoubted supergene replacement.

Occupying, in character, a half-way position between the mutual and graphic structure is the so-called "subgraphic;" this has suggestions of the graphic but lacks the complete graphic pattern.<sup>16</sup>

A common feature of the mutual and graphic structures, and one in striking contrast to the structures of undoubted supergene replacement, is the occurrence of chalcocite in medial positions. In specimen after specimen, the chalcocite, instead of favoring the boundary between sulfide and gangue, is insulated from that boundary by a layer of bornite.

It must be remembered that no deep chalcocite has been found not inmixed with bornite, and that the recognition of the one means the presence of the other. The questions of distribution, then, concern composite areas of bornite and chalcocite. This reopens the questions of the supposed replacement of rock by chalcocite, for that question now becomes the supposed replacement of rock by chalcocite and bornite.

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<sup>16</sup> There is some probability (needing study of more abundant specimens) that the lattice is characteristic of the "central copper zone," which is supposedly that of highest temperature, but absent from the "border zone;" that the graphic is characteristic of both zones; and that the subgraphic may belong still farther out, but yet may not pertain to supergene enrichment. These structures may become serviceable as a thermometer.

It likewise reopens the question of "open space" chalcocite. Does chalcocite, like bornite, replace rock and grow in open spaces? The proof that it does must rest on the assurance that mutual and graphic relations mean contemporaneity.

But what is the chance that the chalcocite replaces, not bornite directly, but such a mineral as klaprotholite, previously replacing bornite?<sup>17</sup> This, though imaginable, lacks affirmative evidence; from the great bulk of replaced ground, the imagined mineral is swept out and only a vestige remains. Experience offers no parallel, and it offers no other sulfide markedly more replaceable than bornite itself. By all reason, if the chalcocite is a replacement, the replaced mineral is bornite.

We are now faced on the supergene chalcocite hypothesis, with an astonishing condition. For the bornite, on the 3000-ft. and on the 1000-ft. levels, in a tight vein and in an open one, is replaced to the same general degree. Part is always gone and part is always left. Except at the vein tops, the relict bornite is too resistant, even under the conditions most favoring supergene replacement; and the replaced bornite is so replaceable that it goes even under the conditions least favorable. Between the relict bornite, on the one hand, and the replaced bornite, on the other, exists a great gulf in replaceability. The relict bornite, moreover, has normal replaceability. For, in the zone of sooty chalcocite, bornite goes to chalcocite with exactly the same ease, compared with pyrite and chalcopyrite, as it does in other districts where supergene enrichment has been studied.

We are confronted now by the old dilemma in a more specific form: *Either the deep chalcocite has replaced an unknown bornite-like mineral of unusually easy replaceability, lying alongside of and intergrown with ordinary bornite, or that chalcocite is hypogene.*

Of the six bornite-chalcocite structures, two mean replacement and four suggest contemporaneity. Where bornite predominates, the characteristic structures are those of contemporaneity; where chalcocite predominates, the structures are those of contemporaneity and also those of replacement. Few polished surfaces fail somewhere to suggest replacement, not of the conventional supergene variety, but of the other sorts here described. Perhaps a quarter of the deep chalcocite is of the replacement type.

### *Intergrowth of Bornite with Chalcocite*

Do the graphic, subgraphic, and mutual structures actually prove contemporaneity? In the deep Butte specimens, the following paragenesis is usual:

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<sup>17</sup> A. F. Rogers: So-called Graphic Intergrowth of Bornite and Chalcocite. *Econ. Geol.* (1916) 11, 582-593.

(1) quartz and pyrite; (2) enargite; (3) bornite and, in minor quantity, chalcocopyrite; (4) chalcocite and covellite.

There can be no doubt, then, that bornite tends generally to be older than chalcocite. But how much older? Is the interval so great as to signify a definite hiatus in deposition? Or is it no greater than that between pyrite and enargite or between enargite and bornite? Is the interval, indeed, of the sort that separates the successive stages of a single process?

The whole question turns on the interpretation of those structures that suggest contemporaneity. So characteristic are they of the bornite-chalcocite relations and so obviously grading into the replacement types, that, proving the graphic and "mutual" chalcocite to be an intergrowth, we could feel confident that the replacement chalcocite was only slightly younger than the bornite. Certain observers have claimed that if part is replacement, all is replacement, even the graphics. Thus, Whitehead:<sup>18</sup>

The bornite of an intergrowth (from Bristol, Conn.) under high magnification is seen to be traversed by very minute veinlets of chalcocite. With extremely high powers, embayments of the chalcocite of the intergrowths are seen to be connected by veinlets ordinarily invisible . . . Etching of the polished surfaces proves that . . . the crystalline structure of adjoining chalcocite embayments is often continuous, and that veinlets between such embayments are entirely continuous with the larger areas of chalcocite.

The conclusion here that all is replacement is not compelled by the facts. Given a waning iron supply, the sulfide deposition could run a systematic course through bornite older than chalcocite, to bornite and chalcocite overlapping, to chalcocite younger than bornite. It is feasible artificially to precipitate two salts A and B in exactly these time relations, and with only a few minutes interval between the oldest A and that part of A which is contemporaneous with the oldest B.<sup>19</sup>

Though we have not found this structure in Butte, we are not relieved of its consideration in a Butte argument. The tenuous veinlets are, indeed, quite in harmony with the observed grosser transitions in Butte between intergrowth and replacement chalcocite. Here, as in the structure described by Whitehead, we accept the proof that part of the chalcocite is a replacement. But we see no compulsion to believe that any of the actual intergrowth is a replacement.

The attempted proof, by the microscope, that the intergrowths mean replacement, is inadequate. What have we to indicate that they mean contemporaneity? In the first place, the waning-iron-supply idea accords

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<sup>18</sup> W. L. Whitehead: *Paragenesis of Certain Sulphide Intergrowths*. *Econ. Geol.* (1916) 11, 7.

<sup>19</sup> These arguments regarding Whitehead's conclusions were first suggested by D. H. McLaughlin in "The Occurrence and Significance of Bornite," a doctor's dissertation, Harvard Univ., 1917.

with the proved paragenesis of the sulfides known to be hypogene. But the graphic and mutual structures are duplicates of structures occurring between bornite and chalcopyrite and between bornite and galena, in which exists no determined general age difference between the bornite and the other minerals: the intergrowths grade into replacements, in which the bornite is alternately older and younger. Furthermore, the graphics are duplicates of alloy eutectics.

The intergrowths between chalcocite and bornite are, by strong presumption, proofs of contemporaneity; they have stood the test of ten years attack; no argument of weight has appeared against them and in no instance is their replacement origin actually proved. On the other hand, in many scores of specimens, contemporaneity has been powerfully suggested, and is made to lie on the side of common sense. As a working rule, contemporaneity has the preference, and only evidence of a highly specific kind could be accepted as proof of replacement.

Yet the hypothesis of two intergrown, polymorphous bornites, one normally and the other extraordinarily replaceable, still leaves the door open to the idea of replacement. This hypothesis will be considered later.

### *Crystal System of the Chalcocite*

Posnjak, Allen, and Merwin<sup>20</sup> found inversion of orthorhombic to isometric chalcocite by two methods. In the first, chalcocite, finely ground, close to 91° showed sharp heat-absorption effects; in the second, chalcocite in rods showed a sudden change in electrical conductivity at about 102°. The discrepancy was assigned to the difference in compactness and the lower figure was accepted. Then, artificial isometric chalcocite cooled down past 91° and, etched on polished surfaces, showed an orthorhombic etch pattern; the isometric-orthorhombic inversion point was thus identified. With more than 8 per cent. of dissolved covellite, no inversion occurs.

Because the temperature 91° lies between the temperature at which we suppose hypogene and supergene chalcocite, respectively, to have formed, these experiments suggest a criterion of origin.<sup>21</sup> Thus, all the observed, natural, faceted crystals of chalcocite are orthorhombic.<sup>22</sup> Yet Merwin has found several octahedral twins 1 cm. long in chalcocite from Kennecott, Alaska, carrying over 8 per cent. dissolved covellite.<sup>23</sup> The suggestion is that the faceted crystals are supergene and that this Bonanza chalcocite is hypogene.

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<sup>20</sup> The Sulphides of Copper. *Econ. Geol.* (1915) 10, 491-535.

<sup>21</sup> Posnjak, Allen and Merwin: *Op. cit.*

W. Lindgren: "Mineral Deposits," 864. N. Y., 1919. McGraw-Hill.

<sup>22</sup> Graton and Murdoch: *Op. cit.*

<sup>23</sup> *Econ. Geol.* (1920) 15, 63; and personal communication.

Conceivably, hypogene chalcocite may form below  $91^{\circ}$ , and even if it formed as isometric crystals above  $91^{\circ}$  it would, through inversion, now be found as orthorhombic, unless—as is not always the case in Butte—it contained over 8 per cent. covellite dissolved. Although isometric form may be proof of hypogene origin, orthorhombic form is no proof of supergene origin.<sup>24</sup>

### *Hypothesis of Two Bornites*

As already stated, the field and microscopic evidence reduces us to a dilemma: Either the deep chalcocite has replaced an unknown bornite-like mineral of unusually easy replaceability, lying alongside of and intergrown with ordinary bornite, or that chalcocite is hypogene.

An ingenious answer to this dilemma is the hypothesis of two polymorphous modifications of bornite suggested by D. H. McLaughlin.<sup>25</sup> According to this answer, the deep chalcocite is a supergene replacement of bornite, independent of the usual controls, but delicately governed by internal structure; the patterns now taken by bornite and chalcocite correspond to an intergrowth between two bornites, one resistant and the other replaceable. On this hypothesis, the deep chalcocite is supergene, but the control of the replacement is hypogene.

This idea of two bornites is based on analogy with other compounds having polymorphous forms, such as  $\text{FeS}_2$ . But the hypothesis, so far as bornite is concerned, is subject to opposition of a chemical and physical nature. In the first place, the contrast in replaceability between the two bornites must be so great that, under no conditions, except those especially favoring undoubted supergene enrichment, is the resistant bornite replaced by chalcocite; and, under all conditions, even those least favoring supergene enrichment, the unstable bornite is totally replaced by chalcocite. Gradational stages in the replacement of the bornite lobes have not been observed; remnants of bornite in the chalcocite lobes and bornite lobes traversed by growing chalcocite stringers do not occur. The supposed replacement either leaves the grains of bornite unaffected or it spreads throughout those grains.

It is conceivable, on an *a priori* basis, that two polymorphous forms of bornite could precipitate simultaneously. But it is doubtful whether two polymorphous forms of a sulfide have been observed as contemporaneous intergrowths. Moreover, from analogy with other polymorphous compounds, the range of condition in which the two forms of bornite could co-exist would be limited and, outside that range, one

<sup>24</sup> For a treatment of this subject in some respects new and not yet well tested on American material, see Hans Schneiderhöhn: "Paramorphosen von rhomb. Kupferglanz nach regul.  $\text{Cu}_2\text{S}$ , Senkenbergiana" (1920) 2, 1-15, and, "Anleitung zur Microscopischen Bestimmung und Untersuchung von Erzen und Aufbereitungsprodukten" (1922).

<sup>25</sup> *Op. cit.*

form would pass over into the other. It is improbable that two bornites could precipitate and persist through varying temperature conditions without one of them undergoing inversion; and such an inversion would develop pressure or shrinkage cracks. The two bornites would differ in density, and if they were in pressure equilibrium at the time of their formation, and one inverted, there would be an increase or decrease in volume. Any expectable evidence of such inversion—for example, a mosaic intergrowth of cracked and uncracked grains—has not been found.

Furthermore, any other direct evidence for two kinds of bornite is not available. The necessary difference in replaceability between the two bornites, as has been shown, is great indeed. That such a difference should actually exist, and never be evident in parallel differences of color, hardness, and susceptibility to chemical attack, is improbable. And that this particular hypothesis, resting on *a priori* grounds, unsupported by direct evidence, and constituting only one among competing hypotheses, should be the correct one, would be a matter of chance only. This chance seems vanishingly small, and the idea of two bornites may be laid aside. With this idea, the sole refuge of the supergene hypothesis disappears.

#### MICROSCOPIC CRITERIA OF ORIGIN FOR BUTTE CHALCOCITE (Commonly but not invariably applicable)

SUPERGENE	HYPOGENE
Control by obvious channels.	Freedom of control by obvious channels, especially the occurrence of medial chalcocite insulated by peripheral bornite, and of chalcocite-bornite mixtures adjacent to clear chalcocite or bornite.
Angular relics of older sulfide, especially in the earlier stages of replacement.	Rounded or corroded relics of older sulfide.
Lattices dependent on visible channelways.	Graphic and mutual structures, lattices independent of visible channelways.
Abundant chalcocite free from bornite.	Bornite widespread through chalcocite and minutely intermixed with it.
Chalcocite occurring with bornite but only in clearly replacement relations to it.	Chalcocite-bornite in contemporaneous relations grading into chalcocite-bornite in replacement relations, where the replacement is not clearly of the supergene sort.

#### SUMMARY

The field argument shows that the deep chalcocite, if it be supergene, must have been produced by the replacement of a sulfide of extraordinarily easy replaceability.



The microscopic argument proves that this mineral must have been hypogene bornite. It proves that no deep chalcocite occurs without the admixture of at least some bornite; that, in part, the chalcocite replaces bornite in peculiar structures non-characteristic of supergene enrichment; and that, in part, the chalcocite is associated with bornite in patterns indicative of contemporaneity. The only remaining refuge for the hypothesis of supergene origin is the assumption that there are two bornites, one having normal replaceability permitting chalcocitization which waned with depth below the capping, and the other having extraordinary replaceability enabling it to be wholly changed to chalcocite even at the lowest mine levels of the district, over 3000 ft. below the surface.

The idea of two such bornites is based on *a priori* grounds and is untenable. The conclusion is that the deep Butte chalcocite is hypogene.

## DISCUSSION

G. M. SCHWARTZ,\* Minneapolis, Minn. (written discussion).—Most of the statements and conclusions of the authors can scarcely be questioned but a study of numerous specimens from Butte and elsewhere has suggested an addition and a modification, as interpreted by the writer.

The paragenesis, as given on page 26, is (1) quartz and pyrite, (2) enargite, (3) bornite and, in minor quantity, chalcopyrite, (4) chalcocite and covellite. Recently, when examining a set of Butte ores containing much enargite it was discovered, on etching the enargite, that tennantite was rather universally present as stringers and veinlets cutting the enargite. The tennantite was clearly earlier than bornite. Thus the paragenesis was: pyrite, enargite, tennantite, bornite, chalcocite. It is noteworthy that the general increase in the copper content was not interrupted, as tennantite has a percentage of copper between that of enargite and bornite.

There may be some question with regard to the statements on graphic intergrowths of bornite and chalcocite. It is stated that the graphic structure was not produced by undoubted supergene replacement and that no instance of their actual replacement has been proved. It is concluded that bornite and chalcocite in graphic intergrowths are contemporaneous.

Specimens studied by the writer from Butte and elsewhere are susceptible of different interpretations. In a specimen from the Leonard mine, chalcocite with residual patches of bornite is cut by many branching veinlets of bornite, which can be seen on polished surface with the naked eye. Under the microscope, graphic intergrowths of bornite and chalcocite are found to be abundant, especially along the contact of the bornite

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veinlet with the chalcocite. It is obvious that the bornite worked out from a tiny crack and replaced the chalcocite and the graphic intergrowths were probably formed in this manner.

Further evidence of replacement and supergene origin was noted in ore from the McGowan mine, Parry Sound, Ont. The ore came from open pits and is composed mainly of quartz-bornite aggregates with some chalcocite and malachite, the latter occurring especially in vugs. The presence of malachite is a strong argument for the supergene origin of the chalcocite. Along the contact between the chalcocite stringers and the bornite are numerous graphic intergrowths. The writer believes them to have been formed by supergene replacement. As far as Butte is concerned, intergrowths of probable supergene origin have not been noted.

In general, it hardly seems safe to conclude that graphic structures necessarily mean a contemporaneous crystallization of chalcocite and bornite and that such structures are never supergene.

## Primary Downward Changes in Ore Deposits \*

By W. H. EMMONS, MINNEAPOLIS, MINN.

(New York Meeting, February, 1924)

Most mineral deposits change as they are followed downward on their dips. Some of these changes are due to primary arrangement; different ores were precipitated at different depths when the deposits were formed. Other changes are due to weathering or secondary enrichment. The chief changes resulting from weathering, in the main, are understood and standard changes are recognized. The processes are relatively simple. They take place at ordinary temperatures and pressures and can be duplicated in the laboratories. Moreover, there are thousands of deposits available for study, because the processes take place near the surface where the development of mines is begun.

The changes due to primary arrangement of the deposits of the metals are not so well understood. Deposition has taken place at higher temperatures and our knowledge of the chemistry of the processes leaves much to be desired. Very few experimental data are available. The deposits, moreover, offer fewer examples because many mines are not developed to depths where the changes can be studied and a change to unprofitable material usually results in stopping work.

Most students of ore deposits now accept, as confirmed, the hypothesis that nearly all lodes and related deposits were formed by solutions originating in intrusive igneous masses. Outward from these masses, the deposits at many places are grouped in zones and the arrangement noted from the intrusions outward are commonly the reverse of the changes noted from the surface downward in a single lode. A study of the changes in groups of deposits, from the parent intrusion outward, will throw light on the changes to be expected in a single lode downward. Because the changes in series of deposits from the intrusive outward may all be observed near the surface, where more data are available, it is possible to increase the number of examples many fold and to apply the statistical method of study with greater confidence of avoiding error.

It is not everywhere possible to identify the parent igneous body to which a group of ore deposits are related. Several kinds of criteria are available; certain groups are superior to others. By applying the

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\* A paper presented at a joint meeting of the American Institute of Mining and Metallurgical Engineers and the Society of Economic Geologists.

criteria that are less likely to result in error and by using only those results obtained and no others, it is possible to follow the steps of the intrusion of an igneous mass and to construct the history of rock differentiation and mineral deposition. By using only those examples that fall within the group of which the parent masses can be identified with least likelihood of error, and by excluding others, the series of changes noted are found to fall into a few groups.

In this investigation, certain areas are given preference. A zone of Tertiary deformation belts the Pacific and extends westward from the East Indies through Asia, Europe, and northern Africa toward the West Indies. In this zone deposits formed at shallow depths greatly predominate. Between this belt, here called the Earth's Hinge Zone, and the six pre-Cambrian Shields, there are six areas, one on each continent, that contain deposits formed mainly in Paleozoic and Early Mesozoic time. These areas are called the Bow Areas, because their belts of deformation and intrusion commonly form bows with the ends bent backward toward the shields. These areas are the most favorable for studies of ore genesis, because they are richly metallized and the rocks and the deposits are not so commonly metamorphosed as those of the shields. Erosion has gone farther than in the Hinge zone, so that the sources of the metals are more often exposed. So far as practicable, the maps of these areas and the literature of the deposits have been studied systematically in formulating and testing a group of working hypotheses.

In the past few years, in connection with professional duties, I have had opportunities to study, in the field, parts of four of these areas, on four continents; and while I personally have mapped only small parts of these preferred areas, the investigations have led me to a greater appreciation of the value of the work that has been done in many remote districts and to a better acquaintance with the literature of the areas containing them. I regret that in a short paper of this nature it is practicable to cite only some of the most important sources of information.

#### CRITERIA FOR RECOGNITION OF A PARENT IGNEOUS MASS WITH WHICH AN ORE DEPOSIT IS ASSOCIATED

*Magmatic segregations* are essentially igneous rocks that are workable for metals. They grade into the parent magmas, and if the deposit was heavier than the parent magma, it will often lie below the remainder of the rock that the magma formed on solidifying. If the segregation was injected into the place it now occupies, its parent magma may be wholly concealed; if so, it is likely to remain undiscovered. On the other hand, rocks that are exposed in the districts containing magmatic injections may be parts of the parent magma from which the injections were derived. If a region includes several districts containing similar deposits, and if all or nearly all of the deposits adjoin, or are found near, a certain

kind of rock, it is rational to suppose that the parent mass is such a rock. Thus Vogt,<sup>1</sup> finding norite and nickel ores in Norway to be almost universally associated, concluded that the norites were the parents of the nickel ores. Subsequent surveys at many other places in the world supported his conclusions. Vogt studied also the pyrite and copper-bearing pyritic ores of Norway and in 26 of 28 districts he found gabbro near the deposits. He concluded that the gabbro was the parent rock of the pyritic deposits. The latter he regarded as igneous intrusions or solidified magmas. Although copper-pyrite intrusions are of subordinate importance in other parts of the world, compared to the lode deposits of copper ore associated with more acid rocks, the associations in Norway seem to be so nearly general that Vogt's conclusions are accepted by many for those deposits.

The association of chromium ore with peridotites is essentially universal and that of platinum with peridotite is nearly so; consequently one is disposed to regard such associations as having genetic significance in new districts where chromium or platinum are found in peridotites, or in the serpentines derived from them.

In general, it is not difficult to identify the parent of a magmatic segregation that was segregated at the place where it now lies. In some districts, there is a whole series of segregations from acid or intermediate rocks to the basic ones that carry the deposits. In the Sudbury district, as shown by Barlow and by Coleman, the nickel ore segregated to the bottom of the mass; subsequently the central part of the laccolithic sheet sank. This type of laccolith is characterized by Grout as the lopolith. When such an intrusion is planed off by erosion, the ores occupying the lowest part of the body will outcrop as a ring around the mass.

On the other hand, many platinum-bearing peridotites in the Urals<sup>2</sup> and also some titaniferous iron ores outcrop as disks surrounded by more acid rocks, which grade into them. The series may be the differentiation products of a laccolithic chamber domed up in the center, but this is obviously difficult to determine except where erosion has gone far, or deep drilling is available. It is possible that certain titaniferous iron ore deposits, like the elongated disk of Routivaare,<sup>3</sup> Sweden, which is known to be relatively thin, have such an origin. The average vertical depth of that deposit, according to Tegengren cannot be estimated to be more than tens of meters. It is possible, also, that some of the larger basic magmatic segregations, differentiated in place, are not in floored chambers (laccoliths, etc.), for that is certainly true of some of the smaller ones like the schlieren and related deposits.

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<sup>1</sup> J. H. L. Vogt: *Zeit. prak. Geol.*, two series of papers in 1893-1895, 1-3.

<sup>2</sup> L. Duparc: *Le platine et les gîtes platinifères de l'Oural. Extrait des Archives des Sciences physiques et naturelles* (March to June, 1911) 31, 1-80.

<sup>3</sup> F. R. Tegengren: "Iron Ore Resources of the World," 2, 584. 1911.

*Pegmatite deposits* are essentially magmatic segregations of the acid type, and the criteria for the recognition of their parent masses are similar to those stated. They are rarely found at the bases of their parent masses, however, but often near their borders. The pegmatite solutions are more mobile and are likely to move farther from their sources.

*Contact metamorphic deposits* are generally found near the rims of the rocks that represent the magma that supplied the materials for

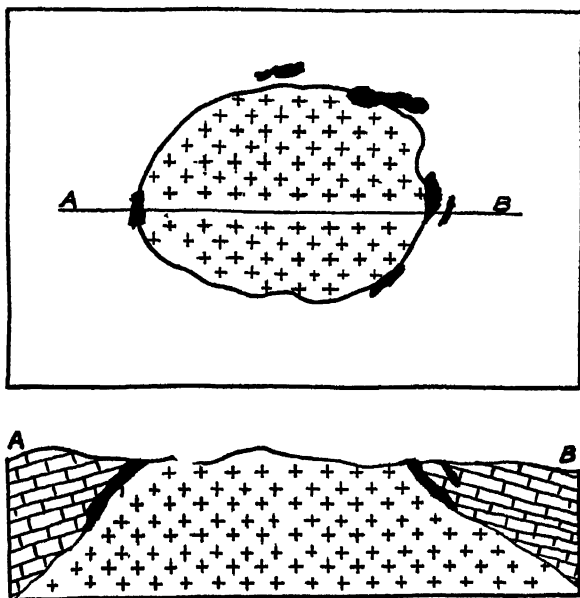


FIG. 1.—PLAN AND CROSS-SECTION OF A DISTRICT SHOWING CONTACT METAMORPHIC DEPOSITS; AREA MARKED BY CROSSES REPRESENTS MAGMA THAT IS BELIEVED TO HAVE CONTRIBUTED THE METALS.

their genesis, Fig. 1. But some are found at a distance from the immediate contact and others replace the intruding rock itself. The latter must be associated genetically with a parent mass below the metamorphosed igneous rock or with a part of the igneous mass that solidified after that containing the deposits had formed.

All of the deposits above mentioned are genetically associated with rocks that cooled slowly. Surface lavas and small dikes rarely, if ever, yield large valuable epigenetic deposits of any type. The flows cool too quickly to differentiate. Small dikes, as a rule, cool quickly and also are too small to supply adequate sources of the metals.

*Mineral veins* and related deposits offer the most difficult problems connected with the identification of their parent magmas. In some districts, veins of a certain type are associated with certain distinctive

rocks. Where this association is sufficiently close and where the number of deposits and of associated rocks is large, the evidence is correspondingly impressive. The method of inquiry is similar to that already mentioned in connection with the magmatic sulfide deposits of Norway.

In certain regions, there are many igneous bodies but the lodes are confined to those rocks that are older than one of the igneous intrusions. The rocks that form the walls of the deposits must have been solid when the deposits were formed and could not have contributed solutions at that stage. It is a reasonable inference that the magma below that which contains the lodes contributed the solutions, or that the liquid mass that cooled to form one of the barren rocks was the parent mass. It is possible, however, that the metals were derived from some deeper mass, no part of which is yet exhumed.

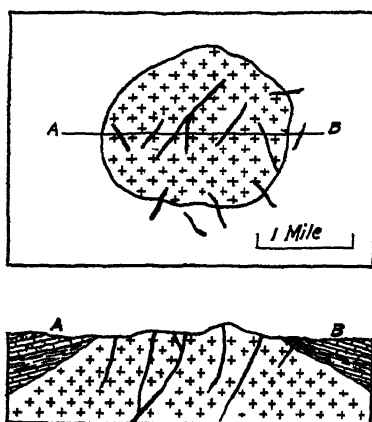


FIG. 2.—PLAN AND CROSS-SECTION OF AN AREA INTRUDED BY AN IGNEOUS BODY WITH LODE DEPOSITS IN CENTRAL PORTION AND NEAR RIMS OF INTRUDING BODY.

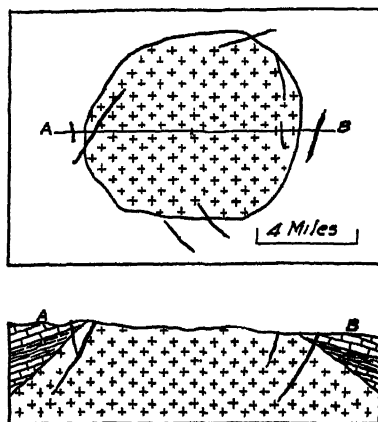


FIG. 3.—PLAN AND CROSS-SECTION OF AN AREA INTRUDED BY AN IGNEOUS BODY WITH LODE DEPOSITS CONFINED TO AREAS NEAR CONTACT OF INTRUDING BODY AND INTRUDED ROCKS.

In many districts, the mineral deposits are closely associated with a single granitic or other intrusion. If the lodes are found in the central part of such an intrusion as well as near the rims, Fig. 2, it is obvious that the metals of the lodes were not derived from the rock now exposed. The deposits were formed after the fractures that they fill and the wall rock must have solidified before the fracturing. It is a reasonable inference that the metals of the veins came from a magma below the rock outcropping, which, however, may be a part of the same intruded unit.

In other districts, the lodes are confined to the peripheral regions, Fig. 3. This is much the more common arrangement in large stocks, except in those that enclose islands or roof pendants of older rocks, and those that are intruded by later igneous bodies. Fig. 2 illustrates a

common type of arrangement in small stocks or batholiths, that have not been deeply truncated by erosion,<sup>4</sup> but one almost unknown in large ones. The arrangement shown in Fig. 3 is the almost universal type in batholiths or stocks more than 15 miles across and one only rarely finds, in districts that contain deposits belonging to one metallogenic epoch, the valuable lodes in the central area, in batholiths with outcrops more than 10 miles wide. Where the lodes are found only in the periphery of the stock, it is a reasonable inference that the barren area in the interior represents the magma that contributed metals to form the lodes. If the

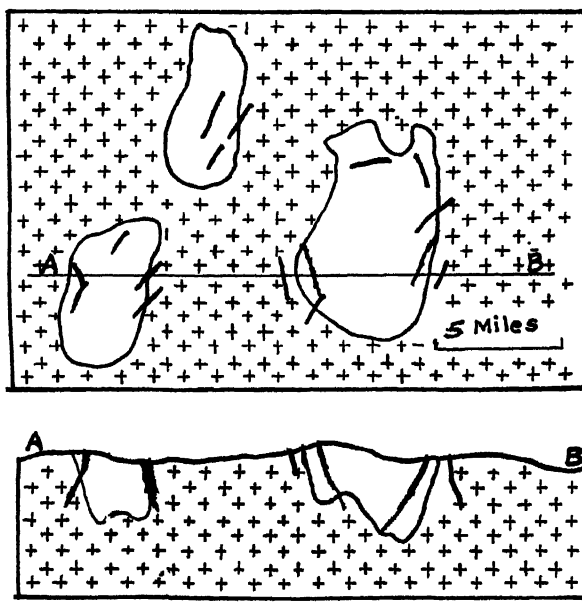


FIG. 4.—PLAN AND CROSS-SECTION OF PART OF AN INTRUSIVE, CONTAINING ISLANDS, BELIEVED TO BE ROOF PENDANTS, NEAR TOP OF A BATHOLITH; DEPOSITS ARE IN AND NEAR ROOF PENDANTS.

interior had been solid when the ores were deposited and if the solutions had come entirely from a deeper seated source, it would be expected that the interior of the intrusive as well as its periphery would contain the metalliferous lodes.

In still other districts, the metals are mainly in the roof pendants or in the islands surrounded by granitic rocks, Fig. 4. In some of these districts, the lodes are found also in the intrusions, but rarely (almost never) more than a short distance from the contacts. It is reasonable to suppose that the magmas which surrounded the roof pendants are the sources of the metals in the lodes which are in or near the roof pendants.

<sup>4</sup> B. S. Butler: Relations of Ore Deposits to Different Types of Intrusive Bodies in Utah. *Econ. Geol.* (1915) 10, 101-122.



In certain districts, there is a well-defined series of deposits passing outward from a center. The deposits of the metals are arranged rudely about a central belt or disk, occupied by outcrops of one or more igneous intrusions. The inference is justified that these intrusions, or others below them, represent the parent masses.

### CHANGES RELATED TO DEPTH

When precipitation takes place from a solution containing many salts, they are deposited in order and the least soluble are deposited first. Thus, it would be supposed that ascending hot solutions, highly charged with mineral matter, would, on entering cooler regions, deposit minerals in reverse order of their solubilities. The solutions are alkaline<sup>5</sup> and the order of deposition is unlike that which is followed when secondary sulfide enrichment takes place, for the waters in the upper parts of sulfide deposits are acid. The secondary changes are related to the changes in composition of the solution rather than to their temperatures. On the other hand, the primary differences are closely related to the physical conditions that prevailed, particularly to the temperatures and pressures.<sup>6</sup> The mineral groups that are deposited at different depths are characteristic. Passing outward from an igneous mass the temperatures decrease, as they go upward toward the surface. Thus the same changes that are found from the surface downward are often shown in reverse order from the batholith outward. The series of changes<sup>7</sup> is reflected,

<sup>5</sup> W. H. Emmons and G. L. Harrington: A Comparison of Waters of Mines and Hot Springs. *Econ. Geol.* (1913) 8, 653-669.

<sup>6</sup> W. Lindgren: Relation of Ore Deposition to Physical Conditions. *Econ. Geol.* (1907) 2, 105-127.

W. H. Emmons: A Genetic Classification of Minerals. *Econ. Geol.* (1908) 3, 611-627.

<sup>7</sup> J. E. Spurr: "The Ore Magmas." N. Y., 1923. McGraw-Hill Book Co. See also an earlier paper by Spurr: A Theory of Ore Deposition. *Econ. Geol.* (1907) 2, 781-795.

R. Sales: Ore Deposits at Butte, Montana. *Trans.* (1913) 46, 3-106.

P. Billingsley and J. A. Grimes: Ore Deposits of the Boulder Batholith of Montana. *Trans.* (1918) 58, 284-361.

R. H. Rastall: Metallogenic Zones. *Econ. Geol.* (1923) 18, 105-121.

R. H. Rastall: Geology of Metalliferous Deposits, 175-201. Cambridge, 1923.

L. DeLaunay: "Traité de Metallogénie: Gîtes Minéraux, etc." Paris and Liège, 1913. Béranger.

W. H. Wong: Mineral Resources of China. *Mem. Geol. Survey of China* (1919) No. 1, 1-270. (In Chinese.)

J. F. Kemp: After Effects of Igneous Intrusion. *Geol. Soc. America Bull.* (1922) 33, 231-250.

W. Lindgren and G. F. Laughlin: Geology and Ore Deposits of the Tintic Mining District, Utah. U. S. Geol. Survey *Prof. Paper* 107 (1919) 1-282.

E. S. Bastin and J. M. Hill: Economic Geology of Gilpin County and Adjacent

not only in the minerals that make up the deposit, but also in the most abundant metals of the deposits; and because opportunities for observation are more often afforded at the surface of the earth, they offer a promising field for investigation. The zones, as expressed by horizontal arrangement, have recently received much attention; and as detailed surveys of many districts become available, they will throw more and more light on the problems of ore deposition.

### SUCCESSIVE ZONES

In many districts, as already noted, the mineral deposits are arranged in series about a parent igneous mass. Where the metals named are present, a common series is: tin, tungsten, arsenic, bismuth, copper, zinc, lead, silver, antimony, mercury. The metals are named approximately in the order in which they occur from the intrusive outward, and in the reverse order from the surface downward. This arrangement depends on the physical conditions that prevail around a cooling igneous mass and on the chemical solubilities of the salts that precipitate from the solutions.

Some of the metals are not named in the series above stated. Iron oxides appear in the series along with copper sulfides, and also with tin and tungsten. Iron sulfides appear everywhere. Gold appears in the series, beginning with arsenic and ending with antimony. In those series containing the largest deposits of tin and tungsten, however, gold is only sparingly present. As Lindgren noted long ago, gold is one of the most persistent minerals, ranging from the region of high temperatures and pressures to those that prevail at shallow depths. The other metals also occur in the series in small amounts at places other than those shown in the normal series, even in the normal development of deposition. They are normally precipitated in largest amounts, however, in the order named. The metals that segregate either chiefly, or altogether, from the basic magmas are: chromite, the platinum group, nickel. On the positions of deposits of manganese and of cobalt, the data are conflicting; that is true also of rarer metals, vanadium and uranium.

### AREAS NOT CONTAINING ZONES

In certain districts, the mineral deposits do not show regular zones. The deposits of the various metals are found here and there without order.

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Parts of Clear Creek and Boulder Counties, Colorado. U. S. Geol. Survey *Prof. Paper* 94 (1917) 1-379.

E. S. Bastin and F. B. Laney: Genesis of Ores at Tonopah, Nevada. U. S. Geol. Survey *Prof. Paper* 104 (1918) 1-50.

J. B. Umpleby: Occurrence of Ore on the Limestone Side of Garnet Zones. Univ. of California Pub. (1916) 10, 25-37.

S. J. Schofield and G. Hanson: Geol. Survey of Canada, *Mem.* 123 (1922) 1-73.

F. L. Ransome and F. C. Calkins: Geology and Ore Deposits of the Coeur d'Alene District, Idaho. U. S. Geol. Survey *Prof. Paper* 62 (1908).

Many other districts show locally only fragments of the normal series. This absence of the common order may be seen: in single veins from the surface downward, in the series passing outward from a magmatic center, or in single lodes passing outward from a center.

The irregularities and reversals in arrangements in the positions of deposits may be due to: (1) overlapping of deposits from two or more magmatic centers; (2) retreat or advance of magmatic centers during one period of deposition; (3) deposition in a single area in different epochs of metallization; (4) other causes not understood.

1. The fluids that carry metals out of magmas move upward to points of less pressure. Most batholiths dip outward. They have rather gently sloping roofs in the main;  $45^{\circ}$  or less is probably the average. Above the roofs are ridges and cupolas; these are the more favorable places for deposition. Many batholiths have two or more ridges or cupolas. The fluids that carry metals rise in the magma to near the walls of the batholiths and then they tend to be deflected upward. They get into fissures and then move outward and upward from the ridges and cupolas. Zones tend to form about the high points, the ridges and cupolas, and the zones from two centers may overlap. Thus there may be a lack of orderly arrangement in deposits formed at the same time. Veins of approximately the same age may cross or join each other so that a lode with ore low in the series will cut one with ore higher in the series, or vice versa.

This explanation accounts for overlapping shown by different veins on the surface; it does not account for reversals in the normal order from the surface downward except where veins cross or join. It is a fact also that overlapping in different veins on the surface is a very common feature in mining districts, but reversals down the dip of veins is much less common. Thus, one rarely finds a large well-defined oreshoot of cassiterite passing gradually downward into one of copper, or a deposit of zinc ore passing into one of lead with depth, although many copper veins pass into tin veins and scores of lead veins pass into zinc.

In some districts, the evidence seems clear that the solutions that deposit the ore have traveled upward through the magmas along the borders of the magmatic chamber to its highest points. There is much evidence that this has happened in the Cornwall and Devon tin fields, where nearly all the deposits are centered about cupolas and ridges. But in many districts certainly deposition takes place also on the sides of the chambers well down from the cupolas, for even the smallest roof pendants, which must once have been at the bottoms of the troughs, are found to contain valuable lodes.

2. Overlapping of deposits may be due also to retreat and advance of magmatic centers. If, during the period of deposition, a magmatic chamber is expanding either by thrust or by stoping, a wave of metalliza-

tion will be superimposed on an earlier one and it will extend farther out. This is brought out by Spurr in papers already cited. If the magma solidifies from the surface downward during deposition, a zone may be superimposed on earlier ones so that the later zones do not extend so far outward; this also causes overlapping. The overlappings due to such processes are not so common as might be expected, however, for as brought out later, nearly all of the epigenetic ores of metals, except iron, are formed during relatively brief periods and after magmas have differentiated to form quartz diorites, monzonites, granodiorites, or granites.

3. Overlapping may be due also to deposition in a single area in different epochs of metallization. Even a feeble metallization superimposed upon an earlier one will result in complications that are often difficult to interpret.

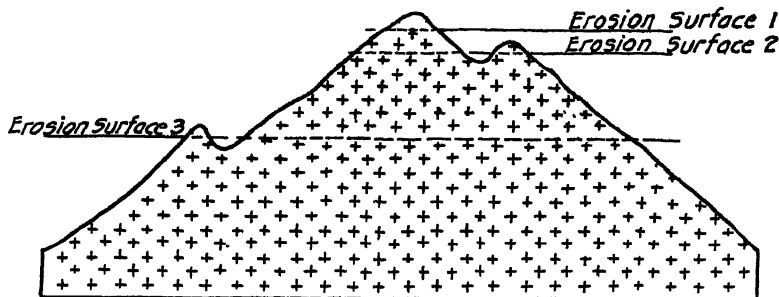


FIG. 5.—SECTION OF A BATHOLITH SHOWING HIGHEST CUPOLA THAT WILL BE EXPOSED ON EROSION SURFACE 1, A HIGH SATELLITE THAT WILL BE EXPOSED ON EROSION SURFACE 2, AND A LOW SATELLITE THAT WILL BE EXPOSED ON EROSION SURFACE 3.

4. Many districts do not show any zonal arrangement of the metals. With a few noteworthy exceptions described later, these include the deposits of the pre-Cambrian shields. The causes are not understood, but one may speculate regarding them and formulate a working hypothesis. There is much evidence that batholithic chambers in general slope outward. Locally, there are reversals of the slope and that gives rise to satellitic intrusive bodies around the larger masses. Erosion will first reveal the ridge of the roof, as shown by surface 1, Fig. 5. This is the "apically truncated stock."<sup>8</sup> Continued farther, erosion will reveal the high satellites as shown by erosion surface 2. Still later the lower satellites are exposed, as shown by erosion surface 3. The zonal arrangements of the metals are best developed in and around the apexes of batholiths and around high satellites. The metals deposited in connection with the lower satellites show the zonal arrangement less perfectly and many of them do not show it at all. High on the batholiths, the fissures are more open and the solutions move more freely to the surface. At greater

<sup>8</sup> B. S. Butler: *Loc. cit.*

depth, the fissures are not so open and connection with the surface is less readily established, and pressures will not vary uniformly. The hypothesis that certain fissures that are filled by veins do not connect freely with the surface was stated by Graton in his treatment of the Appalachian gold deposits.<sup>9</sup>

There is also a separation of metals deep down in the magmatic chambers, for gold deposits are much more abundant than those of other metals, except iron, in roof pendants and around satellites low on magmatic chambers.

In many districts, certain metals of the series are wanting; in others, they are only sparingly present. Certain zones may be only feebly represented, or they may be absent altogether. The solutions that deposit the metals doubtless are different in different places. Certain metals seem to be essentially absent in some of the chemical systems that are given off from igneous magmas.

In some districts of Tertiary metallization, no orderly arrangement in zones appears to be present. Spurr attributes this lack of order to "telescoping" due, in part, to rapid deposition. As recently pointed out by Butler,<sup>10</sup> no entirely adequate explanation of the downward failure of many Tertiary deposits is yet forthcoming. There is a barren zone below the great majority of such deposits and it cannot everywhere be due to the downward termination of the zone of secondary enrichment. It is certainly the most persistent barren zone in the whole series. It appears probable that the rising solutions deposit their loads in the normal arrangement at depth and cease to deposit actively until they approach the surface, where they mingle with ground waters and are cooled, and particularly where gases are allowed to escape. It is probably the presence of the gases that permits the solution to hold certain dissolved metals at relatively low temperatures. The processes have been studied experimentally and discussed by Tolman and Clark.<sup>11</sup>

There are, nevertheless, zones or series fairly well defined in the areas of Tertiary deposition that approach closely the normal type. One of these is in Tuscany, where the order is: tin, iron and copper, a little zinc and lead, antimony, mercury. There is some overlapping, particularly near the end of the series. Another series is shown in northern Italy and southern Austria in the southern Alps. South of a belt of gold, copper, and iron deposits is one of lead; and south of that, a series of mercury deposits. The gold and iron deposits of the first-named belt, however, are, in part at least, probably older than the lead and mercury deposits.

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<sup>9</sup> L. C. Graton: *Reconnaissance of Some Gold and Tin Deposits in the Southern Appalachians*. U. S. Geol. Survey *Bull.* 293 (1906) 60.

<sup>10</sup> B. S. Butler: *Review of J. E. Spurr's paper on the ore magmas*. *Econ. Geol.* (1923) 18, 786.

<sup>11</sup> C. F. J. Tolman and J. D. Clark: *Econ. Geol.* (1914) 9, 559-592.

At Littai, in the southern part of this belt, a deposit carrying mercury near the surface is followed downward into lead ore without mercury.

In Algeria and Tunis, as pointed out by DeLaunay, the Tertiary series is copper and iron, zinc and lead, antimony, mercury. The copper and iron deposits are near the coast; the zinc-lead deposits occupy an interrupted belt south of it; and the antimony deposits, with some scattered mercury deposits, lie in a belt still farther south. These series are instructive for they link the metallization of the Tertiary type with that of older types.

#### RELATIVE VALUE OF CRITERIA

The criteria above enumerated are not of equal value. Where deposits are constantly associated with certain igneous masses over wide areas, it does not follow that the metals of the deposits are derived from the magmas that solidified to form the rocks. Both may have originated from the same source—a magmatic chamber not yet exposed by erosion. That is highly probable if the deposits are in the rocks that formed the intrusive, for the wall rock is older than the lode that it encloses. In areas of later Tertiary metallization, a majority of the deposits are associated with andesites. The andesite in many cases certainly did not supply the metalliferous solutions, for the andesite had already solidified before the deposits were formed. Both were evidently derived from deeper sources.

The criteria that are less likely to lead to error are those that depend on the relations, already stated, that are shown: (1) in areas with deposits of contact metamorphic origin around an intrusive that is not itself replaced by the metallizing solutions; (2) in areas containing intrusives with peripheral lodes, but without lodes in the interiors of the intrusives; (3) in areas with roof pendants or of older rocks surrounded by igneous rocks where all the deposits are in the roof pendants or near them; (4) in areas showing the zonal arrangements approaching the normal series.

If, at first, our studies are confined to those areas where these four groups of criteria may be applied and if we formulate our working hypotheses from the results of those studies and then apply those hypotheses to areas containing other deposits and find them workable, we are least likely to arrive at erroneous conclusions.

#### ROCK DIFFERENTIATION AND ORE DEPOSITION

In the discussions of differentiation in connection with igneous intrusion, it is assumed that differentiation goes on chiefly by falling out of crystals as the magma cools. The light ones rise and the heavy ones sink, and the magma becomes more acid in its upper portion. Daly,<sup>12</sup>

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<sup>12</sup> R. A. Daly: "Igneous Rocks and Their Origin," 436. N. Y., 1914. McGraw-Hill Book Co.

working from the field side, concludes that basaltic magmas are the primary material from which igneous intrusions have differentiated since the time of the oldest known rocks. Bowen,<sup>13</sup> approaching the problem from the experimental side, concludes that "most, if not all, igneous rocks have probably been derived from basaltic magma."

These investigators differ in their conclusions as regards assimilation of the invaded rocks by the magmas. The shapes of the batholiths, however, show that stoping or some similar process has taken place, for many batholiths have nearly flat roofs extending over hundreds of square miles. Many of them cut directly across the strike of invaded beds. The latter are disturbed, but at many places are arched only to a subordinate extent.

At many places we find serpentines derived from peridotites and pyroxenites associated with intrusives. They are often crossed by later granitic dikes. The most basic rocks probably represent the differentiates of the early basaltic or gabbro magma, but some injections are probably originally more basic than normal basalt. The differentiation series is: basaltic-dioritic-granodioritic-granitic-aplitic. The apparent exceptions to the order of differentiation from basic to acid rocks shown by the relations of intrusives in certain districts have been accounted for long ago by Iddings, Cross, Spurr, and others, and need not be reviewed here.

Whether we accept the stoping hypothesis, as developed by Daly, or not, we must accept his conception of the shape of the granitic batholith. Not only is it supported by a mass of field data, which Daly presents, but by many observations in widely separated areas, in reports that have appeared since Daly's early papers were issued. With a few exceptions, those batholiths of which the shapes are known slope outward and the lodes that are associated with them were formed near and above their relatively flat roofs. That conception is, I believe, a vital one for a proper interpretation of the relations of vertical and horizontal changes in lode systems.

The basic and intermediate magmas in the batholith become acid by differentiation. The first minerals to solidify are the ferromagnesian minerals; they are heavier than the magma and fall, leaving a more acid residue. Those parts of the magma that cool at the earlier stages form basalt, if extravasated, and gabbro if injected. The latter are generally dikes, or the marginal phases of the batholith. Later, these basic phases may be destroyed by the rising magma of a still liquid batholith, or they may be intruded subsequently by more acid intrusions.

If the magma breaks through the roof of the batholith at the early stage, basalt flows are formed. The common intrusion which may be

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<sup>13</sup> N. L. Bowen: Later Stages of the Evolution of Igneous Rock. *Jnl. of Geol.* (1915) 23, supplement, 1-91.

regarded as the normal one is represented by Fig. 6. If segregation takes place in the dikes, sills, and larger bodies of basic rock, certain mineral deposits may be separated at this stage. Platinum, osmiridium, nickel, chromium, and segregations of iron may be formed, as well as the non-metallic minerals, asbestos, serpentine, magnetite, or materials that later are changed to form these non-metallic minerals.

The next stage of the batholith is one in which the rocks of intermediate composition are formed. Andesites rise and are extravasated; diorites, and rocks of nearly related composition, solidify around the margins and perhaps in the roofs of the batholith. If the preferred criteria enumerated are applied rigidly we find that this stage is probably the least productive of metals. The diabases, diorites, and andesites are commonly hosts of mineral veins, but the veins have formed at a

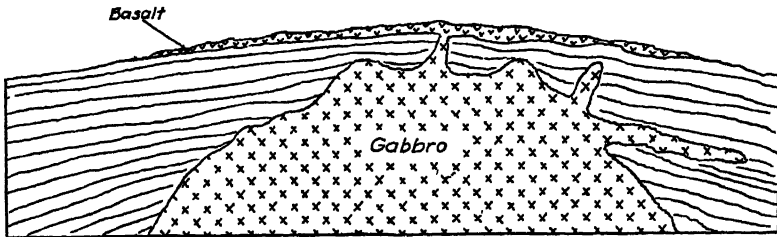


FIG. 6.—SKETCH OF A BATHOLITH OF GABBRO WITH OUTFLOW OF BASALT; SEGREGATIONS OF NICKEL, COPPER, ETC. MAY TAKE PLACE AT THIS STAGE IN FLOORED SATELLITE CHAMBERS LIKE THAT SHOWN AT RIGHT; LINED AREAS REPRESENT INVADDED SEDIMENTARY ROCKS.

later time than the rocks and are believed to be related to more acid differentiates. Nevertheless, a few iron-ore deposits have formed at this stage. The contact metamorphic deposits of magnetite with a little chalcopyrite at Cornwall, Pa., described by Spencer, are in limestone near diabase. The contact metamorphic magnetite and hematite deposits near Brosso and Traversello, Italy, which carry also pyrite, are near a diorite that contains 60 per cent. or less of  $\text{SiO}_2$ . The magnetite deposits of Villa de Trades in Portugal are near a rather basic rock. Many other contact metamorphic iron-ore deposits are known to be associated with rocks that are only slightly more acid than the true diorites. Although certain deposits of iron oxides with a little pyrite and chalcopyrite and probably small deposits of other metals have formed in the early diorite stage, that stage is comparatively unproductive. It lies between the stages when metallic magmatic segregations, such as those of chromium, platinum, etc., are formed and the later stages that are characterized by formation of the lode deposits. The batholith at the diorite stage is represented by Fig. 7. Offshoots at this stage and later ones, however, may yield series of segregations.

In the third stage of differentiation, quartz diorites, monzonites, granodiorites, and granites form. Quartz porphyry dikes are intruded



and rhyolites may be extravasated. The magma may work its way up so that at many places the earlier formed diorite or the gabbro is removed, possibly "stoped" away. At such places, the granitic rock will form the margin of the batholith.

Stopping, which is strongly suggested by relations in many batholiths, is not the only process involved when magmas rise; otherwise a doming

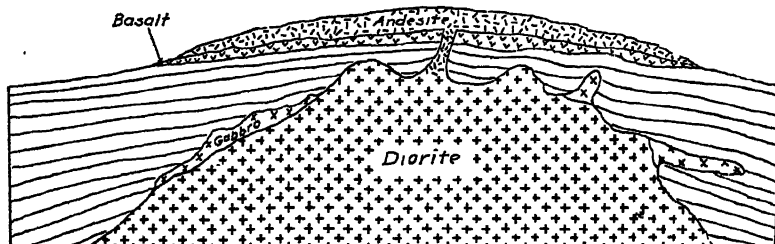


FIG. 7.—SAME AS FIG. 6 AFTER DIFFERENTIATION FROM GABBRO TO DIORITE; ANDESITE IS EXTRAVASATED. A SHELL OF GABBRO REMAINS FORMING PART OF ROOF AT LEFT OF FIGURE. STAGE IS COMMONLY ATTENDED BY DEPOSITION OF IRON-OXIDE ORES WITH A LITTLE COPPER; IT IS LEAST PRODUCTIVE STAGE OF SERIES.

or arching of the cover of the batholiths would not be so common. The magmatic mass often moves; probably the magma itself thrusts up the rocks. This arching is attended by fissuring and commonly by faulting. The movements of the great masses of magmas are opportune, as they take place while cooling and differentiation are in progress. The third stage is represented by Fig. 8.

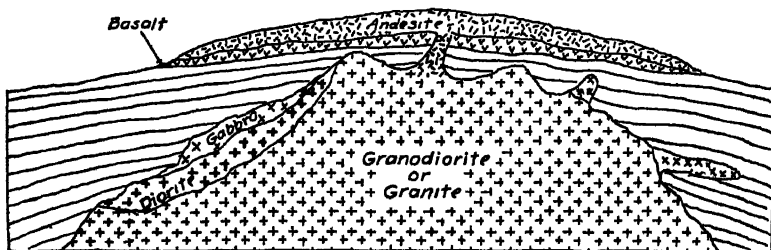


FIG. 8.—SAME AS SHOWN IN FIG. 7 AFTER DIORITE HAS DIFFERENTIATED TO GRANO-DIORITE OR TO GRANITE. AT THE LEFT, A SHELL OF DIORITE REMAINS; ELSEWHERE THE CHAMBER IS EXTENDED. AT THIS STAGE MOST MINERAL LODGES ARE FORMED.

In many granitic batholiths, there are aplites and euries which represent late stages of differentiation of the granites or granodiorites. Some of them form very irregular bodies, like dikes that were intruded before the rocks they cut had completely solidified. They are often cut by the mineral veins and rarely cross the veins and therefore antedate the main period of ore formation. Many deposits are closely associated with these dikes and also with the crystalline porphyries that are offshoots of the main granite masses.

The deposits of the metals form, in the main, in or near the roofs of the batholiths. This arrangement of most of the tin deposits was pointed out by Ferguson and Bateman.<sup>14</sup> Deposition is concentrated in and near the cupolas or the highest parts of the batholiths or in the "roof pendants" of the invaded rocks; that is, in those parts that project downward into the magmas. The diorites and quartz diorites are not uncommonly the

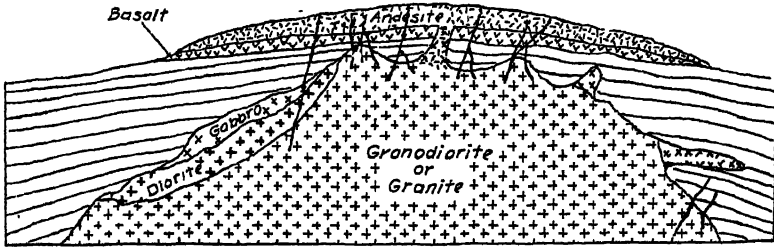


FIG. 9.—SAME AS FIG. 8 AFTER LODES HAVE FORMED IN AND AROUND ROOF OF BATHOLITH.

hosts because these rocks have generally solidified before the more acid granitic phases—the granites and the granodiorites. As a rule, the dioritic rocks form marginal phases and satellites of the larger granitic batholiths. The latter are generally barren in their interiors because their metals have been transferred to and beyond the margins. The great interior masses have remained liquid longer than other parts of the batholith.

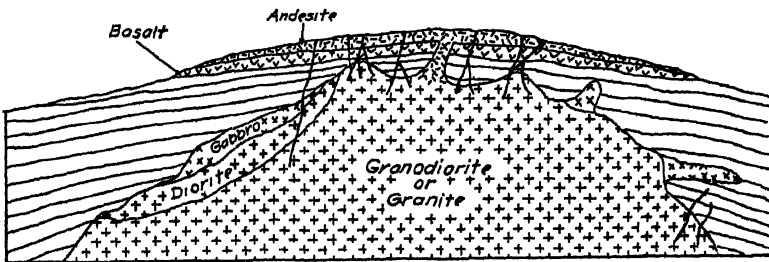


FIG. 10.—SAME AS FIG. 9 AFTER EROSION HAS REMOVED A THIN SHELL OF ANDESITE, REVEALING VALUABLE UPPER PARTS OR HIGHER ZONES OF VEINS.

The final product of differentiation with associated mineral deposits is shown as Fig. 9. It is attacked by erosion. Erosion of only a few hundred feet will often uncover the richer parts of the veins in andesites and associated rocks; this stage is represented by Fig. 10. Deeper erosion, as illustrated by Fig. 11, will remove the tops of cupolas and reveal the deposits that, at many places, are generously deposited in and around

<sup>14</sup> H. G. Ferguson and A. M. Bateman: Geological Features of Tin Deposits. *Econ. Geol.* (1912) 7, 209-262.

them. Such deposits in Utah have been referred to, by Butler, as those of the apically truncated stocks. Further erosion will continue to remove

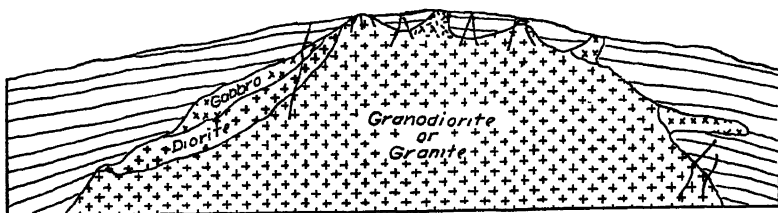


FIG. 11.—SAME AS FIG. 10 AFTER EROSION HAS EXPOSED HIGHER CUPOLAS OR TOPS OF RIDGES ON ROOF; ZONAL ARRANGEMENT IS BEST EXPOSED AT THIS STAGE.

the roof and will expose the lower parts of roof pendants; this stage is illustrated by Fig. 12. A still later stage is one where erosion has



FIG. 12.—SAME AS FIG. 11 AFTER EROSION HAS REMOVED TOPS OF CUPOLAS AND RIDGES; ROOF PENDANTS AND THEIR DEPOSITS REMAIN.

removed much of the main mass; a few scattered veins around the rims remain, Fig. 13.



FIG. 13.—SAME AS FIG. 12 AFTER EROSION HAS REMOVED MUCH OF THE MAIN MASS; A FEW SCATTERED VEINS AROUND THE RIMS REMAIN.

### METALLOGENIC PROVINCES

For the purpose of comparison and study of the earth's mineral deposits, we may recognize thirteen major metalliferous provinces. The greatest of these is the Earth's Hinge Zone,<sup>15</sup> a belt of Tertiary deformation that surrounds the Pacific, and passes west through Asia and Europe from the East toward the West Indies. This belt is about 40,000 miles

<sup>15</sup> W. H. Emmons: "Metallogeny of the Earth's Hinge Zone." Read at the 13th International Geologic Congress, Brussels, 1922.

long. It is the locus of the greatest Tertiary mountain folds, the greatest Tertiary and Recent igneous activity, of the greatest Recent faulting and of earthquake movements. Late Tertiary and Recent volcanism and diastrophism are not confined to this zone, but are greatly concentrated in it. Its rocks are marked by profound unconformities involving all the great systems. It has probably been an area of deformation since pre-Cambrian times. It contains deposits of varied character, but the deposits formed at shallow depths are most prominent; it contains the vast majority of such deposits. It is not unlikely that these deposits lie above buried granitic batholiths which, at most places, are not yet unroofed.

The Hinge Zone is regarded as a belt that divides the remainder of the earth in three blocks, which move independently: (1) the high block that includes Eurasia, the North Atlantic and North America; (2) the intermediate block, which includes Australia, Africa, part of India, South America, and the oceans between; and (3) the low block, which is the Pacific Ocean. Each of the three blocks adjoins the Hinge Zone at or near the East Indies and also near the West Indies. The high block includes three shields: the Siberian, the Scandian, and the Canadian; the intermediate block also includes three shields, the West Australian, the South African, and the Brazilian shields. Each of these shields is a metallogenic province in which deposits of pre-Cambrian age predominate. In the shields, the dominant types of lodes are those formed in and around roof pendants, or in and around batholithic intrusives that are largely unroofed. Such lodes as those so commonly associated with andesites in the Hinge Zone are almost unknown in the shields.

Between each shield and the Hinge Zone, there are areas of closely folded rocks with granitic intrusives. These, in the main, are areas of Paleozoic and in places of early Mesozoic igneous activity. The folds and the belts of igneous intrusions are generally sharply curved. On four of the continents, and possibly on six, they form great bows with the concave sides toward the shields and the convex sides toward the Hinge zone. To facilitate description, they may be designated as the Bow areas.

Suess has described the great series of Paleozoic folds accompanied by igneous intrusions that extends from the western side of the Scandinavian shield southward into Scotland and England, thence east into France where it is developed on the American shield. The area of Paleozoic folding passes east to the Central Plateau, where it touches the zone of Tertiary deformation within the influence of the Alps. To the north and east, it is observed in the Vosges and Black Forest, in the Harz, the Erzgebirge, the Sudettes and Carpathians. In the Carpathians, it coincides broadly with the zone of Tertiary folding of the Hinge. It reappears again in the Urals, thus making a rude U on the south side of the Scandian shield.

The Siberian shield is, likewise, half surrounded by a U of Paleozoic folds. This also was recognized by Suess and has been described and illustrated with maps by DeLaunay.<sup>16</sup>

In East Australia, there is a great bow formed of rocks folded and intruded in the Paleozoic and early Mesozoic time. It lies between the Australian shield of pre-Cambrian rocks extensively developed in western Australia, and the Hinge Zone which passes through New Zealand. These relations have recently been brought out by Andrews.

In South Africa, in the Belgian Congo and North Rhodesia, north of the pre-Cambrian shield of Transvaal and South Rhodesia, is a great area of folding and volcanism, probably late Paleozoic.

In North America, the Appalachian mountains and the Ouachita-Arbuckle-Wichita chain were folded at the close of the Paleozoic and great batholiths of granite were intruded. West of Oklahoma, the Permian and older rocks are buried; but in the Rocky Mountains, in the eastern part of the Hinge Zone, an unconformity between Permian and Triassic rocks shows that the area was folded near the close of the Permian. Thus, there is a bow of Paleozoic folding in North America which corresponds to those of the eastern hemisphere.

In South America, between the Brazilian shield and the Andes, there is a great area containing meridional folds and belts of intrusions of granite that were formed in the Paleozoic time. This area is not mapped in detail, but large parts of it are mapped in reconnaissance; it corresponds to the Bow areas of other continents.

In the shields, the most common geological settings of the mineral deposits are the basically truncated batholiths, the satellites low on the batholithic borders, and the islands surrounded by intrusive rocks which, we have assumed, are roof pendants. The mineral deposits of the shields rarely show zonal arrangements of the metals about the parent intrusives although there are some noteworthy exceptions, mentioned later.

In the Bow areas, the settings mentioned as characteristic of the shields are noted in certain places, but the cupolas and the satellites high on the batholithic chambers are more common. That is because erosion has not gone so far. The zonal arrangement is very common.

In the Hinge Zone, all settings mentioned above are found; but in many districts, the deposits probably are far above their parent batholiths. The zonal arrangement is much less common than in the Bow areas, but is well shown at a few places.

#### RECONSTRUCTED VEIN SYSTEM

A reconstructed vein system is presented as Fig. 14. No vein showing all these changes has been observed, but such probably exist. The ideal

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<sup>16</sup> L. DeLaunay: "La Géologie et les Richesses Minérales de l'Asie." Paris, 1911. Béranger.

vein system is made up of elements of several veins. Some such vein systems probably have a vertical range of 3 or 4 miles, and possibly much more. It is believed that veins showing the metals in the same order, but with three or four of the zones lacking, are common. Many such veins have probably been eroded so that only the lower parts remain.

SURFACE	
Barren. . . .	1. Barren zone, chalcedony, quartz, barite, fluorite, etc. Some veins carry a little mercury, antimony, or arsenic.
Mercury....	2. Quicksilver veins, commonly with chalcedony, marcasite, etc. Barite-fluorite veins.
Antimony...	3. Antimony ores—stibnite often passing downward into lead, with antimonates. Many carry gold.
Gold.....	4. Bonanza ores of precious metals. Argentite, antimony and arsenic minerals common.
Silver.....	Silver minerals, some copper, lead and zinc sulfides, quartz, calcite, rhodochrosite, adularia, alunite, etc.
Barren.....	5. Most nearly consistent barren zone, represents the bottoms of many Tertiary precious metals veins. Quartz, carbonates, etc., with pyrite and small amounts of other sulfides.
Silver.....	6. Argentite veins, complex antimony silver sulfides, stibnite, etc. Galena veins with silver. Commonly silver decreases with depth. Quartz gangue, siderite common, often increasing with depth.
Lead.....	7. Galena veins, commonly with some silver. Sphalerite generally present, increasing with depth. Chalcopyrite common. Gangue is quartz and often carbonates (Fe, Mn, Ca).
Zinc.....	8. Sphalerite veins with some lead and chalcopyrite, quartz, gangue.
Copper.....	9. Tetrahedrite veins, commonly argentiferous, chalcopyrite present. Some pass downward into chalcopyrite. Enargite veins generally with tetrahedrite and tennantite.
Copper....	10. Chalcopyrite veins, generally with pyrite, often with pyrrhotite. The gangue is quartz and in some places carbonates. Some pass downward into pyrite and pyrrhotite with a little chalcopyrite. Generally carry silver or gold.
Gold.....	11. Gold veins with quartz, pyrite, and commonly arsenopyrite and chalcopyrite. At places zones 10 and 11 are reversed.
Bismuth.....	12. Bismuthinite and native bismuth with quartz and pyrite, etc.
Arsenic.....	13. Arsenopyrite with chalcopyrite and often tungsten ores.
Tungsten.....	14. Tungsten veins with quartz, pyrite, chalcopyrite, pyrrhotite, etc. Arsenopyrite is commonly present.
Tin.....	15. Cassiterite veins with quartz, tourmaline, topaz, etc.
Barren.....	16. Quartz with small amounts of other minerals.

FIG. 14.—A RECONSTRUCTED VEIN SYSTEM FROM NEAR BATHOLITH ROOF TO SURFACE.

In many veins, only one of the upper portions (2, 3, or 4), can be observed. Few of these veins have been developed beyond the barren zone, 5. Nearly all of the zones below 5 have been observed at many places grading one into the other. At some places, there are compara-

tively barren zones between them, but such zones are less persistent than zone 5, and generally have less vertical extent. There are many veins that seem to end in essentially barren material—quartz with a little pyrite and other minerals. These barren zones may be found below zones 6 to 14. At many places, zones 7 or 8 are bottomed in barren quartz, in granite, and the barren vein can be followed far into the granite; the zones below appear never to have been developed. On the other hand, where the metals of the lower zones are present in noteworthy quantities, the series in a large number of examples is believed to be approximately that shown by Fig. 14.

The series downward is in the reverse order of the series passing outward from a batholith. The order of the zones is that obtained from a study of: (1) downward changes in many veins; (2) changes in the filling along the strike in veins that strike away from the parent batholiths; (3) changes in the filling of different members of a series of veins in which the series is exposed along a nearly level plane. Such a series, as stated, exhibits changes that are the reverse of those passing downward in a single vein.

As already noted, these zones are most often exhibited in the areas that lie between the pre-Cambrian shields and the Hinge Zone, which is the belt of most prominent Tertiary deformation. They are found at certain places in the Hinge Zone; but generally they are not well shown, probably because erosion has not gone far enough to expose the lower members of the series. The lower members are shown only locally in the shields in the order indicated. The orderly arrangement does not seem to be so well expressed in deep roof pendants, or in and around the small granitic satellites of very large granite batholiths that were formed far down on the limbs of great magmatic chambers.

1. The top of the reconstructed vein is barren. The materials deposited by hot springs and deposits in fissures immediately below them are generally unworkable. Mercury is present, however, in some deposits formed practically at the surface. At Sulphur Bank and Steamboat Springs, mercury has been mined in deposits now forming by hot waters within a few feet of the surface.

2. Mercury deposits are formed not only far above the parent intrusion, but they are probably formed farther from their parent magmas than lodes of other metals. There are no igneous rocks in the Almaden, Spain, which is the world's greatest quicksilver mine. In Kweichow, there is a belt with deposits of mercury ores 300 miles long, extending into Szechuan and western Hunan. Outcrops of igneous rock in this area appear to be wanting altogether. In the south part of the Donetz coal field, Russia in Europe, far from igneous rocks several mines were worked for quicksilver. The Littai deposits in Carniola, south of the Raibl lead district, and the Amiata quicksilver deposits of Tuscany seem

to lie in the ends of zones of metalliferous series. It is noteworthy that in all of these districts (Kweichow, Donetz, Carniola, Tuscany), there are cinnabar deposits in saddle reefs. The rising solutions appear to have halted in the anticlines. At Littai,<sup>17</sup> deposits worked for quicksilver near the surface were worked at lower depths for lead alone.

3. Antimony minerals are frequently found in cinnabar veins. The greatest antimony deposits in the world are those of Hunan, to the southeast of the quicksilver belt in Kweichow, and nearer the granites which, according to Wong, supplied the solutions that deposited both antimony and quicksilver ores. Igneous rocks are not found near the Hunan antimony deposits. In the Central Plateau of France, the antimony ores are associated with granites but relations are not clear, because a Tertiary metallization is superimposed on an earlier Hercynian one.

In Algeria, the antimony ores lie south of the lead-silver ores; at the southern edge of the belt, mercury appears. This has already been noted by DeLaunay. Antimony ores are found at the northern end of the Cornwall mining district, at St. Endellion northeast of Newquay. In several mines, they pass downward into lead ores.

Gold often occurs with antimony ores. The Lucette mine of Mayenne, France, the mines of Villonga, Portugal, the Schönberg and Mileschau region, Bohemia, the Costerfield district in Victoria, and the Hillgrove district, New South Wales, contain deposits of both gold and antimony. Many antimony lodes carry silver, particularly the lodes of Valadou and Mercoeur of the Central Plateau, France. In many antimony lodes, lead increases with depth. Antimony deposits are not so commonly found in anticlines as are mercury deposits, yet such deposits are not unknown; the Arnberg deposits of Westphalia, in the Culm limestone, are probably examples.

4. Gold and silver are rarely found, in commercial amounts, in quicksilver ores, but as already noted they are common in antimony ores. There are many deposits of both metals, however, that contain little or no antimony, and there are certainly some veins of group 4 that were never capped by antimony deposits. The great veins of the gold-silver deposits formed near the surface are almost confined to the Hinge Zone, a broad area of Tertiary deformation that surrounds the Pacific and passes through Asia, Europe and Northwest Africa from the East Indies toward the West Indies. Many of the deposits are in andesite, but the metals have been deposited from deeper seated magmas, probably from granites and granodiorites that are not yet exposed by erosion. Bonanza ores are common and the gangue minerals include quartz, calcite, rhodochrosite, adularia, alunite, barite, etc. Antimony and some arsenic sulfides, more rarely tellurides and selenide minerals, are associated with the precious metals. Galena and sphalerite and a little chalcopyrite are

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<sup>17</sup> L. DeLaunay: *Op. cit.*, 3, 239-240.



present commonly, increasing somewhat downward. Many of the deposits pass into barren gangue with depth.

5. The barren zone that bottoms the bonanza deposits of the precious metals is the most nearly consistent barren zone in the lode deposits of metalliferous ores. At places, barren zones are found to bottom all the groups shown in Fig. 14, but so many precious-metal deposits of the Tertiary type pass downward abruptly into worthless gangue that this has come to be regarded as an outstanding characteristic. The solutions, rising and cooling, deposit the metals in zones lower down often in a fairly orderly sequence. As they approach the surface, they evidently cease to deposit the metals in workable amounts; yet they still carry precious metals, often with antimony and mercury, and they carry also the earthy metals, iron and a little lead, zinc, copper, arsenic and bismuth. When the rising waters reach abundant ground water, they are chilled. Gases that, as shown by Tolman and Clark, hold the metals in solution, will readily escape because the fractures communicate freely with the surface that is not far away. Cooling and escape of gases and, for certain metallic sulfides, the dilution of the solution will cause precipitation. The residue of the metals in the rising waters is thrown down at comparably shallow depths in zones 2 to 4. The solutions must be almost depleted of the valuable metals before they reach the surface, for most waters of hot springs, as well as hot-spring deposits, contain but little mercury, antimony, or precious metals.

6. Silver veins, with gold and with stibnite, tetrahedrite and complex antimonates, and silver veins with some galena and sphalerite, are found commonly near the borders of batholiths. In depth, some of them carry more galena and sphalerite and less silver. The gangue differs from that of the silver-gold veins of group 4. Adularia and alunite are absent. The Granite-Bimetallic vein at Philipsburg, Mont., is in granite near the west border of the Philipsburg batholith; it carries silver and some gold in a quartz gangue. Stibnite and arsenopyrite are present in the primary ore and silver sulfo-salts of antimony and arsenic abound in the enriched ore. Eastward, the vein system can be followed far toward the center of the granite batholith; the vein matter consists of quartz and some pyrite and is nearly barren. Westward, parallel veins of the same system pass into sedimentary rocks where they carry silver with much rhodochrosite. Many other silver-lead veins are found in or near the Boulder batholith, which lies to the east of the Philipsburg batholith. Some of these veins, as shown by Knopf, carry tourmaline and were formed at fairly high temperatures. In the silver veins and silver-lead veins, sphalerite generally becomes more prominent with depth, and with it chalcopyrite often appears. There are not, however, commercial deposits of either of these metals in some of the veins of this group. They pass downward into material that is unworkable. In some veins,

the system, Fig. 14, ends in granite, essentially at zone 6, with a feeble representation of 7 and 8 and the lower representatives of the series are wanting altogether. Some deposits of galena pass downward to chalcopyrite ores without a zone of zinc between. In Cornwall, zinc is not very abundant, although there are several mines that contain considerable amounts. The zinc ore is, in general, below the lead-silver ore, above the copper ore or tin ore, and its presence was favorably regarded in prospecting. There was a miner's dictum: Black Jack rides a big horse. The Wheal Mary Ann, which lies to the southeast of the Bodwin Moor granite, is one of the largest lead-silver lodes of Cornwall. It passed downward, according to Dewey, directly into copper ore.

7. Many deposits of galena carry silver in large amounts. Galena ores also commonly carry sphalerite. Near the surface, the silver is concentrated by weathering and secondary enrichment will often mask the changes due to primary arrangement. Sphalerite is much more readily dissolved than galena. A homogeneous silver-lead-zinc deposit will commonly yield, on weathering, one showing from the surface downward: (a) lead ores rich in silver, (b) lead ores lower in silver, (c) zinc ores with some lead and silver. We find, however, series of veins passing outward from a granitic mass with zinc predominating in veins near the mass and lead and silver farther out. The series shows that zinc is deposited nearer the intrusive than is lead. The primary arrangement from the surface downward (silver, lead, zinc) is accentuated, however, by secondary enrichment.

8. There are many examples of argentiferous galena veins that pass downward into sphalerite veins and sphalerite veins that pass downward into pyrite or chalcopyrite veins. These have been summarized by Billingsley and Grimes. The series, galena, sphalerite, low-grade pyrite, named in order is shown at Castle Mountains and at Little Belt, Mont. (Weed), and at Neihart, Mont. (Sales). In the Clausthal district, Germany; at Pontgibaud, France (Lodin); and near Argeleze Gazost, Pyrenees, sphalerite succeeds galena (Vogt). In the Wood River district, Ida., the series is: rich silver, galena, poor ores with more pyrrhotite, pyrite and sphalerite (Lindgren); in the Coeur d'Alene, Ida., rich silver, galena, poorer ores with pyrrhotite, pyrite, and sphalerite (Ransome). At Przbram, Bohemia: galena, sphalerite, chalcopyrite, pyrite, arsenopyrite (Schmid). In the Great Retallic vein, east of the Cligga Head-Mt. Agnes granites of Cornwall, the series is: galena, sphalerite, copper (Dewey). At Bingham, Utah, passing toward the igneous mass, the series is galena, sphalerite, chalcopyrite, and pyrite. (Perry, Locke, and Bateman.) Many other examples could be cited. The barren vein matter that is commonly found between certain other zones appears often to be wanting between zones 7 and 8.

9. Tetrahedrite is a common associate of silver veins and it appears in the series above 9. There are some veins, however, that are worked for

copper, in which tetrahedrite is the principal ore mineral. At Tizi-Hemed, Algeria, 25 km. southeast of El-Azouar, and at Mauzaia, Algeria, 25 km. southeast of Blida, tetrahedrite ores change downward to chalcopyrite ores. This zone is placed here with some hesitation, however, because tetrahedrite decreases in depth in some zones above 9.

Enargite is placed below zinc blend. In the series at Butte, as shown by Sales, a central zone with enargite and with little or no sphalerite is surrounded by one in which sphalerite is rarely absent from the copper ores. It is probably higher in the series than chalcopyrite. At Tintic, according to Lindgren and Laughlin, the lodes in monzonite carry pyrite and some chalcopyrite and enargite. In the sedimentary rock, one mile north of the contact, enargite is abundant.

10. Chalcopyrite veins are the most abundant sources of primary copper ores. Nearly all of them contain a little gold or silver. Pyrite, pyrrhotite, or both, are commonly present in considerable amounts. The gangue is quartz. Carbonates are present in some of the deposits, but in many of the largest deposits carbonates are essentially absent. Many of the deposits carry zinc and, at places, zinc ores pass downward into copper ores. In many mines of the Cornwall-Devon region, chalcopyrite veins pass downward into tin veins. In the Levant mine, in and near the Lands End granite mass, one of the few mines still working, tin ore is found below copper. In the Lands End district, veins followed on strike away from the granite show decreasing tin and increasing copper. In Cornwall, this series downward is shown in many of the lodes. The series at the surface approaching the granite, shown in different lodes around several different batholiths, is: silver, lead, zinc, copper, arsenic, tungsten, tin. Many copper lodes elsewhere, however, and some in Cornwall pass downward into quartz and low-grade pyrite and there is no evidence that other metalliferous zones succeed them in depth.

11. Of all the metals treated in the reconstructed vein system, gold offers the greatest difficulties. It is abundant in zone 4 and appears, generally, in subordinate amounts in all the zones between 6 and 12. The gold-silver veins of zone 4 differ greatly from the gold deposits of zone 11. The former are the "young gold veins;" the latter are the "old gold veins," long ago recognized by Vogt and by Lindgren in his treatment of the precious-metal provinces of North America. The deeper veins of zone 11 almost invariably carry auriferous pyrite; commonly chalcopyrite and arsenopyrite are present. The arsenopyrite is often very closely associated with the gold. Galena, sphalerite, and tetrahedrite are not unknown, but are usually subordinate and silver is ordinarily much less abundant than in the deposits of zone 4. The chalcopyrite deposits commonly carry gold and some of them carry it in considerable amounts. Although there are few chalcopyrite deposits that are worked downward to auriferous pyrite deposits, the position

of the zones is probably as indicated. Perhaps a pyritic zone with some chalcopyrite and some gold should be recognized between 11 and 12. In a few deposits, also, the gold seems to be deposited farther from the parent magma than the copper; zones 10 and 11 are reversed. With respect to tin, the relations are clearer. Where gold and tin are found together, the gold is deposited at greater distances from the magma than tin.

Gold is unique among the metals shown in Fig. 14, in that it is deposited lower down on the walls of large batholiths than others. Gold deposits are, by far, more abundant in small deep roof pendants than deposits of the other metals.<sup>18</sup> That is the most impressive thing about the distribution of the older gold veins. It is illustrated in scores of groups of veins in Western Australia, Rhodesia, and Canada, and in certain other shields. Although a few deposits are known, tin ore is less common in roof pendants. Other metals are associated with the gold and there are a few valuable deposits of copper, zinc, lead, and silver in roof pendants. There is evidence, however, of a separation of metals in the magmatic chamber; gold, with other metals in smaller amounts, is deposited well down on the walls, while much gold and most of the other metals on segregation tend to move to the cupolas and ridges of the roofs of batholiths. Nevertheless, where gold and tin are deposited in the same series around the cupolas of granitic intrusions, the tin deposits are nearest the intrusives and the gold deposits farther away. There are many examples of this arrangement and there seems to be no exception.

12. Bismuth ores are commonly associated with those of copper, tungsten, and tin. Bismuth ores commonly carry gold and silver. The bismuth zone is tentatively placed below copper and above tungsten and arsenic, but there are not enough clearly described occurrences to warrant its accurate definition.

At Maymac, Central Plateau, France, ores worked for bismuth carry copper, tungsten, and a little tin. Bismuth veins, with tin and tungsten, are found in the Erzgebirge and in Bolivia. The bismuth deposits of Whipstick, New South Wales, are among the most productive in Australia. A flat-roofed granite batholith intrudes Devonian sediments. The deposits are found in "pipes" in granite near the roof, sloping with the granite contact. Metals won include molybdenum, bismuth, and precious metals in a quartz-feldspar gangue. At Kingsgate, New South Wales, in similar deposits described by Pittman, bismuth ores are associated with the same metals and with tungsten. The copper-gold deposits at Balhannah, South Australia, pass downward into copper-bismuth ores. At the Shepherd and Murphy mine, Moina district, Tasmania, described by A. M. Reid, bismuth ore with bismuthinite and native

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<sup>18</sup> Deposits of iron oxides, not included in the series, often form in similar positions.

bismuth, occurs mainly within 100 ft. of the surface below which tin and tungsten ore with some bismuth are mined.

13. Arsenic is found in large amounts associated with ores of copper, particularly in enargite veins, and arsenic minerals are present in many deposits of the precious metals. The position of arsenopyrite where zones are well defined is with tungsten below the zone of copper and above that of tin; that is shown for many of the veins of Cornwall and Devon. In the Tavistock district, the cinder from ores that had been roasted for arsenic was reworked recently for tungsten. In China, much of the tungsten produced in recent years was from old waste piles of arsenic mines and from the cinder of roasting plants.

14. Tungsten minerals are found in gold-quartz lodes formed at moderate depths. Examples are those of Atolia, Calif., described by Hess and of Nederland, Colo., described by George and by Bastin; and deposits of the Black Hills, S. Dak. The bulk of the tungsten ores, however, comes from deep-seated lodes where the tungsten is generally associated with tin. A belt extending from north of Tavoy, Burma, through Siam to the Malay States, is the most noteworthy. Other examples include the deposits of Cornwall, the Western and Central Plateaus of France, of the Erzgebirge, Southern China, Eastern and Northern Australia, Tasmania, Bolivia and many others. In Cornwall and Devon, the series from the deep levels up is: tin, tungsten and arsenic, copper. This order is recorded by Dewey in many of the largest lodes.

In certain deep-seated tungsten deposits in or near granite, tin ores appear to be lacking. Examples are found in LaToma district, Argentine.

15. Copper veins pass downward into tin veins and, as already noted, arsenic and tungsten commonly appear in the lower part of the copper-bearing zones and play out in depth where tin predominates. In Cornwall, the series from the granites out is, approximately: tin, tungsten, arsenic, copper, zinc, lead, silver, antimony. Across the Channel, in Western France, there is a group of tin and tungsten veins of the same age associated with granites north of which are lead-silver deposits. Still farther north is a deposit of mercury. The zones are feeble and not clearly defined. In the Central Plateau, there are evidences of the horizontal zones; but in the central and eastern part of the Plateau, the Paleozoic metallization is complicated by a later Tertiary one and relations are not clear. In the southern part of the Plateau, there are well-defined zones of zinc and lead, but tin deposits are unknown.

In the Erzgebirge, approximately, the same series is shown as in Cornwall.<sup>19</sup> In the Riesengebirge, to the southeast, as pointed out long

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<sup>19</sup> W. Petrascheck: Metallogenic Zones. *Econ. Geol.* (1928) 18, 777-778.

In addition to the metals of Cornwall a little quicksilver is found northwest of Freiburg.

ago by Krusch, there are zones with gold, copper and zinc; but tin deposits are lacking. The series of zones in Tuscany, as shown by De-Launay, is approximately the same as in Cornwall although the tin deposits are small. In Vallongo, near Oporto, Portugal, the series is: (1) tin (some tungsten), (2) lead, (3) antimony and gold.

South China, according to Wong, exhibits probably the greatest examples in the world of successive zones around a central parent magma. The series is: (1) tin, tungsten, and molybdenum; (2) zinc, lead and silver; (3) antimony; (4) quicksilver. In eastern Australia, there is a belt of granite trending north from Tasmania to Queensland. Tin deposits are found at scores of places. In Queensland, west of Cairns, Stannery Hills yields tin and Wolfram Camp yields tungsten; both are near the border of a great granite intrusion. To the north, a few miles away in the invaded rocks, are the Thornborough and Hodgkinson gold districts.

Tin ores are found in a large number of the deposits in the New England district of New South Wales. The reports by Andrews, Wilkinson, and others show that the tin deposits are related to the granites, particularly to the Third granite which is highly siliceous, and to its late eutritic phases. In and near the granite are deposits of tin, tungsten, molybdenum, and bismuth. Farther out are ores of copper, lead, and antimony. Some mercury is found near the antimony deposits. Parts of this series are shown at many places.

In northwestern Tasmania, as shown by Twelvetrees and Ward, the series is: (1) cassiterite; (2) pyrite, some stannite, chalcopyrite, and sphalerite; (3) argentiferous galena with siderite; (4) silver, with antimony sulfides. This series or parts of it are shown at several places.

The eastern Australian and Tasmanian deposits are in the Bow area of Paleozoic deformation and intrusion. Along the north coast of Australia are many tin and tungsten deposits, which are believed to be pre-Cambrian. In the Woggamon district, 110 miles southeast of Port Darwin, the tin deposits are found around five or six granite masses. Out farther from the tin deposits, as shown by Jensen, Gray and Winter, are many gold deposits and some of copper. In the Agicondi district, which adjoins the Woggamon district on the southeast, a granite mass is nearly surrounded by a series of smaller granitic intrusions. Tin and tungsten ores are found near the granites at many places and gold deposits are found farther away. The larger granite mass almost surrounds a body of the intruded rock, which contains many deposits of gold, among them the saddle reefs of the Pine Creek district. In the Marranboy district, about 75 miles southeast of Pine Creek, valuable tin deposits with tourmaline gangue are found in a basin of tuffs almost rimmed by granite intrusives.

In the northern part of Western Australia, granite masses are intruded in the pre-Cambrian. The granites, in general, are barren but along

their margins are deposits of tin, gold, copper, and some of antimony. Near Pilbara, as shown by Woodward, three zones are well defined: (1) a tin-bearing zone near the granite, which has yielded considerable stream tin; (2) an auriferous zone farther from the granite, with quartz veins that have supplied large nuggets of placer gold; and (3) chalcopyrite veins, some of which carry galena.

These tin-gold districts along the northern coast of Australia are noteworthy, for districts showing well-defined zones are rare in the pre-Cambrian shields, although they are very common in the Bow areas.

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#### DISCUSSION

J. E. SPURR, New York, N. Y. (written discussion).—This paper is, in the main, an elaborated restatement of the zonal theory of ore deposition which I proposed in 1907.<sup>20</sup> At that time I wrote:

I now submit further that there results from the consolidation of the pegmatites and the pegmatitic quartz veins, practically all the accumulated water in the magma; that with this water is associated a greatly accumulated (concentrated or magnetically differentiated) quantity of the highly mobile and solvent elements such as fluorine, boron, and chlorine, whose presence in granite and pegmatite magmas is shown by such granitic and pegmatitic minerals as tourmaline, mica, and apatite; that much silica is present; and that there are also present many valuable metals, constituting a large portion (in some instances by far the greater portion) of the whole amount contained in the original body of magma.

I submit that from such a residual magma quartz veins of later origin than the quartz veins closely allied to pegmatites are deposited, and that in them valuable metallic minerals are deposited; that from these veins a further residue results, still fluid under such conditions, but subject to partial consolidation (or to phrase it differently, precipitation) at a later period, under different conditions, involving chiefly a lowering of temperature; and that many successive stages of precipitation follow, the final stage being when the water has lost most of its heat, and has left behind nearly all the elements with which it was associated, and to whose mobility and concentration it was so important; and, finding its way to the surface, mingles with the great body of surface and shallow-seated waters which has been so plausibly regarded as the accumulated residue of all crystallized magmas.

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<sup>20</sup> *Econ. Geol.* (1907) 2, 781-795.

The successive stages, according to the theory I present, are marked by differences of earthy minerals, but more delicately, perhaps, by changes in the metallic minerals.

This is the origin of most mineral veins and other forms of ore deposits, including ores of lead, zinc, copper, silver, gold, bismuth, antimony, arsenic, and other metals. Thus while pegmatites and pegmatitic quartz veins usually occur in or very close to the earlier consolidated rocks, the successive stages migrate farther and farther away from the metallic hearth (the zone of differentiation); which, in general, means that they are successively deposited nearer and nearer the surface. Thus the successive stages can be recognized as successive vertical zones of ore deposition.

A preliminary attempt, open to much revision, may be made to define some of the principal zones, beginning from the bottom:

1. The pegmatite zone, containing tin, molybdenum, tungsten, etc., with characteristic gangue minerals, such as tourmaline, topaz, muscovite, beryl, etc.
2. The free gold-auriferous pyrite zone, with coarse quartz gangue.
3. The cupriferous pyrite zone.
4. The galena-blende (galena usually argentiferous) zone.
5. The zone of silver and also much gold, usually associated with metals which combine with them to make substances which are undoubtedly highly mobile, and account for the relatively elevated position of the zone. These associated metals include antimony, bismuth, arsenic, tellurium, and selenium. Characteristic minerals of this zone are tellurides and selenides of silver, gold tellurides, argentiferous tetrahedrite and tennantite, polybasite, stephanite, and argentite.
6. The zone of earthy gangues, barren of valuable metals. I believe it will be ultimately possible to subdivide these periods.

I reiterated the theory in 1909,<sup>21</sup> and again in 1912,<sup>22</sup> and at length in 1923—in the last-named year, in "The Ore Magmas," where I discussed it at length. In 1912 I wrote as follows:

In the original paper on ore deposition above referred to (*Econ. Geol.*, Vol. 2, No. 8, p. 791, Dec., 1907), the writer made a preliminary attempt to define the principal zones of ore deposition; adding that it would probably be ultimately possible to subdivide these periods. He now submits a modified column, based on experience in the last four years.

A. The pegmatite zone, containing tin, molybdenum, tungsten, etc., with characteristic gangue minerals, such as tourmaline, topaz, muscovite, beryl, etc.

B. The free gold-auriferous pyrite zone, with coarse quartz gangue. (Principal gold zone.)

C. The cupriferous pyrite zone. (Principal copper zone.)

D. The zone of argentiferous pyrite and auriferous arsenopyrite. Either one may be represented to the exclusion of the other, indicating a subdivision of this zone. Silver may fall in the pyrite and gold in the arsenopyrite. (Principal arsenic zone.) A frequent mineral of this zone is pyrrhotite. Antimony may occur, especially as jamesonite. In certain metallographic provinces ores of nickel and cobalt occur in this zone. The ores of this zone are frequently without gangue.

E. The blende zone. (Principal zinc zone.)

F. The argentiferous galena zone. Silver may fall in the galena. (Principal lead zone.)

G. The zone of silver and also much gold, usually associated with metals which combine with them to make substances which are undoubtedly highly mobile, and

<sup>21</sup> *Econ. Geol.* (1909) 4, 318.

<sup>22</sup> *Econ. Geol.* (1912) 7, 485, et seq.



account for the relatively elevated position of the zone. These associated metals include antimony, bismuth, arsenic, tellurium and selenium. Characteristic minerals of this zone are tellurides and selenides of silver, gold tellurides, primary argentiferous tetrahedrite and tennantite, polybasite, stephanite and argentite. (Principal silver and gold zone.)

Inspection of the vein column shown on p. 983, and comparison with the two I have just cited, shows that it is essentially the same. At the top of the column, the author has added arsenic and antimony, which while undeniably in general shallow formed, I am inclined not to regard as belonging to the general sequence of ore magmas, as I have explained.<sup>23</sup>

The author (p. 966) refers the nickel ores of the Sudbury district to segregation by sinking to the bottom of a norite sill. This old explanation has been shown to be without foundation.<sup>24</sup> The orebodies in the Creighton mine, for example, pass from norite through later granite without breaking their continuity.

On p. 980, the author describes as the greatest of the earth's metalliferous provinces "a belt of Tertiary deformation that surrounds the Pacific, and passes west through Asia and Europe from the East toward the West Indies. . . It is the locus of the greatest Tertiary mountain folds, the greatest Tertiary and Recent igneous activity, of the greatest Recent faulting, and of earthquake movements." In 1905,<sup>25</sup> I called attention to the metalliferous belt which rings the Pacific Ocean:

The significance of the geographic coincidence of these different phenomena, occurring on so stupendous a scale as to stand out unmistakably from the confusion of detail of the world's geology, has yet to be thoroughly understood. These geographically coinciding phenomena may be summed up as follows: (1) the borders of the earth's greatest ocean; (2) the most persistent of the earth's lofty and bold mountain belts; (3) the belt of the earth's most active and extensive recent vulcanism; (4) a belt showing similar recently erupted lavas; (5) a belt showing similar lavas erupted during the Tertiary; (6) a belt of enormous and roughly uniform later Tertiary mineralization, involving great concentration of silver and gold.

The author's extension of this belt from the East to the West Indies is interesting, concerning which we may hope to hear more later; also of his conception of these belts as a "hinge zone," which divides the earth into three great blocks. Concerning all this, we shall be able to judge when his full argument is published.

I am inclined to question the scheme of rock differentiation given on pp. 976-980. According to this, the granites solidify after the basic rocks. Yet it is more the rule than the exception that basic dikes are the last phase of a granitic magmatic sequence.

The most valuable feature of the paper is the great amount of data the author has compiled as to the zonal distribution of ores. The list is

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<sup>23</sup> "The Ore Magmas," 2, 842.

<sup>24</sup> "The Ore Magmas," 2, 567.

<sup>25</sup> Geology of the Tonopah District. U. S. Geol. Surv. *Prof. Paper* No. 42, 286

not complete but is the most elaborate presentation yet made. But the significance of some of the cases cited is probably doubtful. There are too many complications in ore deposits that gleaming the literature is apt to range unlike cases into a single category. It may happen, for example, that deposits formed at distinct periods may be reported as displaying a change from one to another with increasing depth.

W. H. EMMONS (author's reply to discussion).—The first part of the discussion has to do with the matter of priority for the so-called "zonal arrangement" of metals. The paper cited the first contribution (1907) from which Mr. Spurr quotes, also the last (1923). I regret that in so short a treatment I could not take up the literature more fully; this deficiency to some extent Mr. Spurr has remedied. I find also that I have not noted DeLaunay's<sup>26</sup> first paper on the subject, which appeared in 1900, in which he gives the series of metals genetically related to granitic intrusives as: (1) tin, bismuth, molybdenum, most closely related; (2) lead, zinc, silver, nickel and cobalt, less closely related; and (3) the bonanza type of gold deposits and mercury deposits, still farther away. This is, I believe, the first actual statement of a series. In 1913, De Launay developed the series more fully in *Les Gîtes Minéraux*. In 1904, Waller<sup>27</sup> attempted to give for a series in the Heemskerk field, Tasmania, a kind of quantitative basis. His zones, passing outward from the granite, are: (1) a contact zone with magnetite and cassiterite; (2) a zone in which pyrite and sphalerite predominate; (3) a zone with siderite, lead, and silver and some antimonial ores.

Waller showed, by diagram, the abundance of various minerals in the several zones and his correlations were supported by Twelvetreets and Ward, who reported on the district, in 1910, and reproduced his diagram.<sup>28</sup>

The subject of mineral zones interested students of ore deposits at a very early date. Most of the investigators, however, did not interpret the observations in the light of the solubilities of the metals in depositing solutions, which seems to be the most probable explanation of the series.

Primary gradations are recognized in the first edition of Beck's textbook<sup>29</sup> on ore deposits, and in most of the texts on ore deposits that have since appeared.

Probably no one, however, has given so much emphasis to the importance of the subject as has Spurr in his *Ore Magmas*, which appeared in

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<sup>26</sup> L. DeLaunay: *Les Variations de Fillons Metallifères en profondeurs*: *Rev. Gén. des Sci. Pures et Appliquées* (1900) 11, 575.

<sup>27</sup> G. Waller: Report on the Zeehan Silver-lead Mining Field: *Tasmania Geol. Surv. Bull.* (1904) 24.

<sup>28</sup> W. H. Twelvetreets and L. K. Ward: The Orebodies of the Zeehan Field. *Geol. Surv. of Tasmania, Bull.* 8, (1910) 72. The original paper by Waller is not accessible to the author.

<sup>29</sup> R. Beck: "The Nature of Ore Deposits." Trans. by Weed, New York, 1905.

1923. He gives (p. 611) a series for the intermediate magma: molybdenum, tungsten, gold, copper (silver), zinc, lead (silver); and one for the siliceous magma: molybdenum, tin, tungsten, copper (silver), zinc, lead (silver). In these sequences, tin and gold are placed in different series.

In a discussion of the series (p. 444) he says:

The association of gold ore with granite is far more general than in the case of tin, but since both occur characteristically associated with siliceous rocks, why do they not occur together? Not only do they not do so commercially, but they hardly touch mineralogically.

I believe that tin and gold can reasonably be placed in the same series, for gold is found in the majority of tin-bearing regions, and gold deposits are commonly associated with tin deposits so closely that they appear to have been derived from the same magmatic source. In the Carolina tin belt, gold and tin deposits are closely associated; gold is found in the Jones tin mine, and cassiterite is found in the Brewer gold mine. In Nova Scotia, the granite with which the gold deposits are associated contains the New Ross tin mine.

In Cornwall, gold is only rarely found; but across the Channel, in France, gold deposits and tin deposits occur near granites that probably belong to the same province as the Cornwall granite.

In southern Africa, gold deposits and tin deposits are closely associated at several places. In Katanga, the well-known Ruwe gold mine is at the southern end of the belt of granites of the Bia Mountains, which are associated with many valuable deposits of tin. The Embabaan tin field, in Swaziland, is near the Forbes Reef gold field.

Gold and tin deposits are found near the same granite masses in Australia: Woggamon, Agiconde and Pilbara near the north coast have been mentioned. Along the east coast, the association is noteworthy in Queensland, in the Herberton field northward to the Palmerville gold field. To the south, the gold and tin deposits near Brisbane seem to be related to the same granitic intrusives. The same relations are found in eastern New South Wales.

Although gold deposits are commonly found associated with the tin-bearing granites, there are many large gold-bearing areas where tin deposits are wanting: western Ontario, eastern Ontario, and western Quebec; the main gold field of western Australia, excluding Greenbushes, southern Rhodesia, etc. All of these fields are areas of deeply eroded granite batholiths. The gold deposits are almost never found in the granite, except at places near intruded schists and most of the deposits are in the schists. The auriferous areas commonly contain molybdenum deposits and a few large copper deposits appear. Lead and zinc ores are rare, and antimony is generally only sparingly present. These deposits

were all formed low down on the walls of batholiths or near the edges of small satellites low down on the walls (Fig. 5). The tin deposits much more generally are formed higher up and, therefore, they are rarely exposed in areas exhibiting deposits of metals in roof pendants surrounded by great areas of granite.

Referring to the origin of the Sudbury nickel deposits, I can claim no great familiarity with the field, although I have studied certain areas along the contact of the eruptive, and have visited a few of the mines. I am convinced of the truth of the hypothesis of Coleman, Barlow, and others; namely, that the deposits have formed by segregation at the base of the sill. The fracturing of the wall rock along the contact and the cementation of the fragments with ore do not prove that mineral solutions deposited the ore. Aqueous solutions may have played a small part in the depositional processes, for even sulfide magmas formed by gravitational separation are probably not entirely dry. If the mineralized granite adjoining the deposit is really the Killarney granite, there may have been absorption, or even a later feeble period of mineralization, although the Killarney elsewhere near its contact is marked by the deposition of arsenopyrite and gold, rather than nickel ore. Viewing the entire field, the nickel deposits are too closely associated with the edge of the eruptive to be attributed to metallization attending the granite. The best possible test of Coleman's hypothesis was made by Roberts and Longyear, who studied the geology of the area, drilled the contact, and found large deposits of ore below the drift in the area along the southeast border of the eruption.

I make no claim to authorship of the "zonal theory." For several years I have been engaged largely in testing it, particularly with a view to ascertaining its limitations. With this object in view, I have studied certain areas in the field, but naturally I have had to rely mainly upon maps and reports of others. The method employed is possible only because in recent years so many excellent geological maps have been issued. Briefly, the mineral zones are rarely developed in the shields, they are not rare where deep erosion has laid bare the batholiths of the hinge zone, and in the areas between the latter and the shields the zones in normal order are common, although at many places certain metals are either lacking or are sparingly present.

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## Oxidation and Enrichment at Ducktown, Tenn.\*

[*Secondary Enrichment Investigation Contribution No. 16.*]

BY GEOFFREY GILBERT, A. M., CAMBRIDGE, MASS.

(New York Meeting, February, 1924)

THE material that forms the basis of this paper was collected in the spring of 1922, during a ten-day visit to Ducktown by the writer in the company of Prof. L. C. Graton. The time available for the work was far too short to allow anything like a thorough study of the deposits, and structural and stratigraphic questions, though they have an important bearing on the origin of the primary ores, were necessarily left untouched. Attention was focussed on the zone of oxidation and enrichment; and by devoting most of our time to the upper levels, open pits, and old workings, and examining the deeper levels only thoroughly enough to obtain a fair idea of the nature of the primary sulfide ore, we were able to make a reasonably complete survey of the various orebodies.

With this field work for a background, the writer later made a study, in the Harvard laboratories, of the specimens obtained during the visit. As some of the facts brought to light by this study appear to be new, it seems worth while to set forth the outstanding features and a proposed explanation of them.

Much of the Ducktown material that is obviously of greatest significance, as regards oxidation and enrichment, is soft and crumbly. Notwithstanding the desirability of gaining from such material all possible information as to its mineral composition and textural relationships, but little has heretofore been learned regarding it; but, by suitable preparation of this material in connection with the present study, it has been possible to examine it under the microscope without any disturbance of its texture and about as satisfactorily as if it were hard, fresh ore. The information thus gained has contributed measurably to the results set forth in this paper.

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\* A paper presented at a joint meeting of the American Institute of Mining and Metallurgical Engineers and the Society of Economic Geologists.

## GENERAL DESCRIPTION

The Ducktown deposits have been adequately described by Henrich,<sup>1</sup> Kemp,<sup>2</sup> Weed,<sup>3</sup> Emmons and Laney,<sup>4</sup> and Taylor,<sup>5</sup> and only a very brief résumé of the main facts need be given here. The district, which is in the extreme southeastern corner of Tennessee, has been producing copper intermittently since about 1850. The ore first mined was from a thin, but very rich, zone of secondary sulfides, which was worked on a small scale for a number of years and was an important source of copper for the South in the Civil War. Later (about 1889), the lower grade primary ores began to be exploited, at first for their copper alone, but in recent years with sulfuric acid as an important byproduct. The gossan has also been used at times as an ore of iron. There are at present two active companies: the Tennessee Copper Corp., operating the Burra Burra and London mines, and the Ducktown Sulphur, Copper and Iron Co., whose chief mine is the Mary. The district produced 16,727,803 lb. of copper in 1920, and 15,084,294 lb. in 1921 (equal respectively to 1.38 and 2.98 per cent. of the total United States production). The total production to the end of 1921 is given as 398,553,000 lb. During the dull period of 1921, when most of the big western mines were shut down, the demand for sulfuric acid was sufficient to keep the Ducktown smelters operating at nearly full capacity.

Ducktown lies near the eastern border of the geological province known as the Appalachian Valley. To the southeast, the Blue Ridge, carved by the mature erosion of pre-Cambrian gneisses, rises in a tangle of rugged hills. To the northwest are the straight parallel ridges of the Upper Paleozoic formations. Between these lies a belt of Cambrian sediments, metamorphosed into schists, which have produced a sort of intermediate topography, less rugged and intricate than the Blue Ridge but far less regular than the structural ridges to the west. Through this schist belt the Ocoee River, a part of the Tennessee River system, flows with a general northwest course. The present level of the river at Ducktown is about 1500 ft. The hills around it rise from 500 to 2000 ft. higher, but it is bordered by a relatively flat basin of variable width with a general elevation of 1700 to 1900 ft. This basin, according to LaForge,<sup>6</sup> is a remnant of the Cumberland peneplain (pre-Cretaceous

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<sup>1</sup> C. Henrich: Ducktown Deposits and Treatment of Ducktown Copper Ores. *Trans.* (1895) 25, 173.

<sup>2</sup> J. F. Kemp: Deposits of Copper Ores at Ducktown. *Trans.* (1902) 31, 244.

<sup>3</sup> W. H. Weed: Copper Deposits of the Appalachian States. *U. S. G. S. Bull.* 455 (1911).

<sup>4</sup> W. H. Emmons and F. B. Laney: Mineral Deposits of Ducktown, Tenn. *U. S. G. S. Bull.* 470 (1911).

<sup>5</sup> J. H. Taylor: Pyrite and Pyrrhotite Resources of Ducktown, Tenn. *Trans.* (1918) 59, 88.

<sup>6</sup> L. LaForge and W. C. Phalen: Ellijay Quadrangle. *U. S. G. S. Folio* 187.

or early Cretaceous); or to be more exact, it represents the advanced stage of erosion that the region near the watershed had reached at a time when the land nearer the sea was a true peneplain. It is in this basin, drained by the Ocoee and by its tributary Potato Creek, that the Ducktown district is situated.

The schists underlying the basin are derived from clastic sediments—conglomerate, sandstone and shale, for the most part highly siliceous—named by the Survey geologists the Ocoee series and referred by them to the Lower Cambrian.<sup>7</sup> The rocks have undergone close folding, some thrust faulting, and severe metamorphism, so that they now appear as quartzites, quartz and mica schists, graywackes, etc., with both bedding and schistosity approaching the vertical. The structure, which is broadly synclinal, has been worked out in detail, and various folds and cross faults have been mapped, but the shortness of our stay precluded any attempt to deal with areal problems.

### PRIMARY ORE

The deposits are lenses of heavy sulfides in schists, somewhat similar in type to those found elsewhere along the Appalachians, notably in Virginia, Vermont, and Quebec. The lenses occur in two series running parallel to the strike of the schists, and each lens conforms to the schists in strike and (at least approximately) in dip. The ores are composed predominantly of pyrrhotite, chalcopyrite, and sphalerite, with a variable amount of pyrite and a rather scanty gangue of quartz, calcite, tremolite, and numerous other silicates. The ores from Burra Burra and Mary are worthy of detailed description; first, because these mines are, at present, the chief producers and, second, because they represent two extremes between which the ores from most of the other mines lie.

At the Burra Burra, the most distinctive feature is the abundance of pyrite. The typical high-grade ore from this mine has a noticeably "porphyritic" appearance, the "phenocrysts" consisting of pyrite crystals and the ground mass of pyrrhotite, chalcopyrite, sphalerite, and gangue. The pyrite crystals range from  $\frac{1}{16}$  in. up to (exceptionally) 4 in. on a side. Some are cubes with sharp edges, but usually they exhibit a certain amount of rounding and corrosion by the enclosing sulfides. The ground mass contains numerous smaller crystals of pyrite, blebs of glassy quartz and of calcite, needles of amphibole, and grains of magnetite, all surrounded by the later sulfides, pyrrhotite, sphalerite, and chalcopyrite. Of these pyrrhotite is by far the most abundant and, in general, the earliest to form; the sphalerite is younger and the chalcopyrite younger still. The three minerals, however, are often intergrown so complexly that it is difficult to establish any definite sequence; in

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<sup>7</sup> Arthur Keith: Nantahala Quadrangle. U. S. G. S. *Folio* 143.

fact, it is safe to say that they are nearly contemporaneous and that there has been much overlapping in their formation. The gangue minerals, except for some chlorite, appear to be earlier than the sulfides.

The country rock is normally a quartz schist, composed of predominant quartz, an acid plagioclase, and biotite, with accessory titanite, rutile, garnet, zircon, muscovite, tremolite, zoisite, and diopside. All of these are earlier than the sulfides, but it is, generally, hard to decide which of them belong to the ore period and which are original or products of regional metamorphism. The original rocks were impure siliceous sediments, and most of the quartz, feldspar, and biotite were present before the ore-forming period. The feldspar, much of which is untwinned albite, is generally fresh and scarcely ever sericitized. As for the biotite, some of it is bleached in proximity to sulfides, while some occurs in sulfide veinlets or along the borders of sulfide masses in such fashion as to indicate that it belongs to the ore period. Garnet, also, was probably formed both by dynamic and hydrothermal processes. Amphibole is chiefly an ore mineral, as are zoisite and diopside. There is a great deal of chlorite associated with the sulfides, some of it earlier but most of it later. The sulfides replace the earlier minerals, attacking feldspar more actively than any other. The genetic sequence appears to be about as follows: gangue (except chlorite), magnetite, pyrite, pyrrhotite, sphalerite, chalcopyrite, chlorite.

The Mary ore contains practically the same minerals as that of Burra Burra, but in very different proportions. Pyrite, instead of being nearly as abundant as pyrrhotite, is scarce. There is less calcite and less quartz, and tremolite becomes the chief gangue mineral; chalcopyrite and sphalerite are present in, roughly, the same amounts as at Burra Burra. These are the only really common minerals in the orebody, but locally garnet and zoisite are found in large crystals. The general sequence is about the same as at Burra Burra; namely quartz, silicates, and calcite, then pyrite, pyrrhotite, sphalerite, and chalcopyrite, the last three overlapping. In both cases, it is certain that by far the greater part of the gangue was formed before the deposition of the sulfides, though there is no distinct break and no doubt that both ore and gangue are the result of a single series of events.

The ores from the London, Isabella, Eureka, and Old Tennessee mines are much like the two types described and, in general, are intermediate between them. Pyrrhotite is always the most abundant of the sulfides, but locally large amounts of pyrite are found. Quartz, calcite, and tremolite (or actinolite) are everywhere the main gangue minerals and the only ones that are really abundant, though others such as garnet are very widespread.

At two other mines, the dumps of which we examined, the East Tennessee and No. 20, a great deal of diopside was seen. It occurred



at the East Tennessee in very large crystals and appeared to be one of the main constituents of the ore.

The tremolite, it must be admitted, is often found in the sulfides in sharp prisms that show no corrosion and leave a clean-cut mold when they are broken out. This is the only thing noted by the writer that suggested overlapping in the deposition of the sulfides and gangue. Even in this case the prisms are often broken and the cracks filled by sulfides, and as a rule it is beyond doubt that the tremolite is the earlier.

The specimens of low-grade ore and impregnated wall rock show, beyond doubt, that the ore minerals replace schist. Whether the high-grade ore is also a replacement of schist is another question, for in the heavy sulfides nothing remains that can be definitely classified as unreplaced rock. The glassy quartz that forms a large part of the gangue might be interpreted as recrystallized residual material. The calcite and lime silicates, however, must be otherwise accounted for, as there is little or no lime in the country rock. Either it has been introduced with the ore or it is derived from a more limy bed of the sedimentary series. The second explanation is favored by Emmons.

Finally, it should be emphasized that whether the ores are entirely a replacement of the normal schist of the region or whether included lenses of limestone have been the chief subject of attack, there is no reasonable doubt as to the epigenetic character of the deposits. Their mineralogy and their relation to the wall rock show clearly that they were formed, at high temperatures and probably under heavy load, after the major part of the metamorphism of the surrounding rocks had been accomplished.

## SURFACE ALTERATION

### *Gossan*

The orebodies are capped by a heavy gossan up to 100 ft. in thickness and often very pure. The ore of the larger lenses consists of sulfides with a comparatively small amount of gangue; and when the sulfur is oxidized off, the calcite dissolved, and the silicates decomposed the residue consists almost wholly of iron oxides with a little quartz and kaolin. A great deal of gossan, averaging 40–50 per cent. iron, has been shipped at different times as an iron ore. Limonite is, naturally, the principal constituent, but some of the polished sections showed fairly large amounts of a lighter mineral, whose color in reflected light is intermediate between the gray of normal limonite and the pure white of hematite. In the present day, when limonite has ceased to have a definite mineralogical significance and has come to be a general term signifying ferric-oxide monohydrate with a variable amount of water,<sup>8</sup> it is perhaps inaccurate to say that this

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<sup>8</sup>Posnjak and Merwin: The Hydrated Ferric Oxides. *Am. Jnl. Sci.* (1919) [4] 47, 311.

lighter mineral is not limonite, but at any rate it appears to be an iron oxide with a rather low degree of hydration. The gossan shows a great variety of structures, ranging from earthy material that was, obviously, formed by the alteration of sulfides *in situ*, on the one hand, to lacy, woody, stalactitic, and botryoidal forms that imply transportation of iron in solution, on the other. The color varies from yellow brown to red brown, deep red, or nearly black, with red brown predominating.

### *Zone of Enrichment*

Below the gossan lies the zone of secondary sulfides, the "black copper" that was exploited in the early days of the camp. This zone is remarkable (or rather was remarkable, for it is almost wholly a thing of the past) for its thinness, richness, incoherence, and the definiteness of its upper and lower surfaces. Before describing this zone, it may be as well to explain that the amount of black copper we saw was very small indeed; the greater part of it was removed 50-70 years ago. The pockets were cleaned out by primitive methods but with extraordinary thoroughness. Furthermore, what little the miners left has been largely obliterated by mine oxidation; that is, by the greatly accelerated oxidation resulting from the opening of the pits, the artificial lowering of the water level, and the free admission of oxygen. However, many of the old workings are still accessible, and an occasional small pocket in the walls can be made to yield specimens of black copper, while the position of the workings in itself throws light on the relation of the enriched zone to the gossan and to the primary ore.

Apparently, the zone was not continuous; and in many places there can be seen an abrupt change from unaltered sulfides to solid gossan. In some of the pits is exposed massive primary ore, rusted on the surface by mine oxidation but almost perfectly fresh when broken into. Within a vertical distance of 2 or 3 ft., or even of a few inches, this goes over into normal gossan without a particle of sulfide; in places there is almost literally a knife-edge contact. Only along major fractures does the limonite extend for any distance into the sulfides; and major fractures, or minor ones for that matter, are not at all abundant in this ore. This direct change from primary ore to gossan holds for large parts of the orebodies, but at other places, wedged in between them, were pockets or blankets of black copper. Henrich<sup>9</sup> describes it as follows:

The zone contained rich copper ores, distributed in patches of varying dimensions (but not as a continuous body) within a zone or layer extending more or less horizontally across the vein, in thickness varying from 2 to 8 ft., and more, above the sulfuret orebodies and below the gossan. Such a deposit would, at times, extend over the whole width of the orebody from wall to wall and for long distances along the strike. If of such horizontal extent it was also usually of considerable depth. In

<sup>9</sup> *Op. cit.*, 206.

other places, the black copper would be found only in small pockets or seams of limited extent and then usually along one or other of the walls of the ore deposit. Detached deposits of such ores would also occur more in the center of the ore deposit.

The ore was undoubtedly rich. There has, perhaps, been a tendency to exaggerate its richness; much of it is said to have run over 40 per cent., and figures of 50 and 60 per cent. are mentioned for particular pockets. A more conservative estimate was given by Whitney,<sup>10</sup> writing at a time when development was going on vigorously. He says (apparently speaking of the Ducktown mines in general):

The percentage yield of copper is usually low; but the purest portions contain from 20 to 30 per cent. of metal.

And again:<sup>11</sup>

Beneath the gossan is found a bed or mass of black cupriferous ore, of variable thickness and width. . . . It is a mixture of black oxide of copper with the sulfuret and some siliceous or earthy matter. There is also considerable sulfuret of iron, in small crystals and fragments, scattered through it, as well as some sulfate of copper. . . . Its yield, as prepared for shipment, is from 20 to 25 per cent., although it varies very much in its composition in different parts of the same mine. . . . At one place in the Hiwassee mine, the body of black ore was stated to be 45 ft. in width, and the veins are said in some places to expand to much greater dimensions. The thickness of the black ore is equally irregular with its width. In some places, it is accumulated in conical masses from which many hundred tons of ore, nearly pure, are taken. When the veins were first opened I estimated its average width on the whole extent of the vein at 10 ft., and its thickness at 2.

The black copper was at first supposed to be a mixture of oxides and sulfides, and no doubt a certain amount of oxide, and even of carbonate, was mined, but the chief mineral was undoubtedly chalcocite. The ore was very crumbly and much of it could be removed with a shovel. The crumbly specimens we obtained were badly leached and sulfatized, but from them it appears that the most important minerals of the secondary zone were chalcocite, covellite, and a secondary iron sulfide, which will be discussed later.

The gossan, as already stated, varies in thickness from 100 ft. down to practically nothing. The bottom of the gossan, which is also the zone of enrichment and the top of the primary sulfides, is roughly parallel to the surface, but is found at the greatest depth in the higher ground and closest to the surface in the creek bottoms; indeed Potato Creek has, in one or two places, cut through into the primary ore. There is thus a distinct relation between the position of the enriched zone and that of the water table. Whether the zone is at, above, or below the present

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<sup>10</sup> J. D. Whitney: *Changes in Mineral Veins near the Surface, with Particular Reference to the East Tennessee Copper Mines.* *Am. Jnl. Sci.* (1855) [2] 20, 53.

<sup>11</sup> J. D. Whitney: *"Metallic Wealth of the United States."* Philadelphia, 1854. Lippincott; London, Trubner & Co.

ground water level, there is enough similarity between the two profiles to force the conclusion that they are connected. Whitney pointed out this variation in the depth of the gossan and stated that the shafts reached the black copper at about the point at which water was struck.

## MICROSCOPICAL STUDY OF ALTERATION

### *Oxidation*

In attempting to study the enrichment, the writer has given attention to the whole subject of the change that the ore undergoes in passing from its primary state to gossan. These changes take place within such a short distance that suites of specimens running from practically unaltered sulfides to clear gossan were easily obtained. Specimens illustrating the enrichment were much more difficult to get; and many that were collected in the belief that they contained black copper proved to be nothing more than crumbling iron sulfides thickly coated and impregnated with soluble sulfates. Unsatisfactory as some of the results were, a fairly clear idea of the alteration processes was finally reached.

The chief mineral of the deposits, the one most easily oxidized and most readily affected by sulfuric acid, and the one that appears to play the most important part in the process of enrichment, is pyrrhotite. It will therefore be dealt with first.

The first change that the ore undergoes as the surface is approached is the development of small amounts of a secondary mineral, believed to be marcasite, in veinlets cutting the pyrrhotite. It is cream-colored in reflected light, with hardness high; so far as the microchemical tests go it might be either pyrite or marcasite. It shows, however, none of the tendency to develop definite crystals, which is so noticeable in the primary pyrite. Closer to the gossan, the pyrrhotite begins to crack and break up, becoming more and more pitted and difficult to polish. Simultaneously with this comes the formation in large quantities of a secondary iron disulfide replacing the pyrrhotite. This has been identified as marcasite for the following reasons:

1. Its color in the hand specimen is a pale yellow, paler than that of normal pyrite.
2. In the closed tube, it gives abundant sulfur and a magnetic residue.
3. A pycnometer determination, made on about 2 gm. of coarsely crushed material which appeared under the binocular to be pure, gave its specific gravity as 4.89. This is low for pyrite (which is usually over 5) but about right for marcasite. However, according to Stokes,<sup>12</sup> the density is not a reliable criterion for distinguishing the two minerals.
4. No crystal faces, except some very small doubtful ones, were observed, but botryoidal forms are common.

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<sup>12</sup> H. N. Stokes: On Pyrite and Marcasite. U. S. G. S. *Bull.* 186 (1901).

5. Under the microscope it behaves like marcasite. It is creamy white, with hardness high, is affected by  $\text{HNO}_3$ , and is negative to the other reagents. Marcasite is supposed to be attacked by  $\text{HNO}_3$  rather more strongly than pyrite; in this case, the amount of attack depends largely on the texture of the mineral. The hardest material is not browned much more than ordinary pyrite, while the duller spongy stuff is blackened rapidly and is also affected by KCN and KOH.

6. All the evidence points to the fact that the solutions from which the mineral was deposited were acid, perhaps strongly so. The results obtained at the Geophysical Laboratory<sup>13</sup> indicate that under conditions of low temperature and moderate or even low acidity, marcasite will form rather than pyrite. While none of these reasons can be regarded as conclusive it seems that as between pyrite and marcasite the probabilities are strongly in favor of the latter.<sup>13a</sup>

The pyrrhotite, under the influence of surface solutions, usually reveals parallel planes of weakness—presumably cleavage planes—along which the solutions work and along and from which the marcasite forms. Many good examples were seen of grains that were originally pyrrhotite, bordered by hard firm marcasite and cut by parallel bands of marcasite to form a sort of grating, while the spaces between the bars are either cavities or filled with some soft material. The proportion of hard to soft varies greatly; in some grains nearly the whole interior is rotten while in others it is chiefly firm marcasite. In some cases, there is a gradual change in the nature of the material; the marcasite at the grain borders and along the cracks is hard and white while farther in it is softer, browner, and more easily affected by reagents.

In many cases, instead of forming this grating structure, the marcasite works outwards with a smooth front from cracks or from points along cracks, forming spheroids or ellipsoids in the pyrrhotite. These spheroids, which are sometimes strikingly developed even in comparatively fresh ore, usually show one or more concentric cracks, as if there had been some loss of volume during their crystallization. The marcasite near the center is often denser than that on the outside; and the contact with the surrounding pyrrhotite is usually represented by a narrow space, as if some soft material had been removed in polishing. Occasionally, the pyrrhotite is found in actual contact with the borders of the spheroids;

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<sup>13</sup> Allen, Crenshaw, Johnston and Larsen: The Mineral Sulphides of Iron. *Am. Jnl. Sci.* (1912) [4] 33, 169.

<sup>13a</sup> Since the completion of this paper some tests have been made on the mineral with reflected polarized light. So far, no evidence has been obtained that it is doubly refracting. If it is pyrite, it should show no double refraction. Some specimens known to be marcasite do show polarization; but sufficient work has not been done to determine whether or not all marcasite does so. For the present, the writer remains of the opinion that the balance of evidence favors the conclusion that the material under discussion is marcasite rather than pyrite.



FIG. 1.—VEINLETS OF MARCASITE REPLACING PYRRHOTITE; MARY MINE.  $\times 100$ .

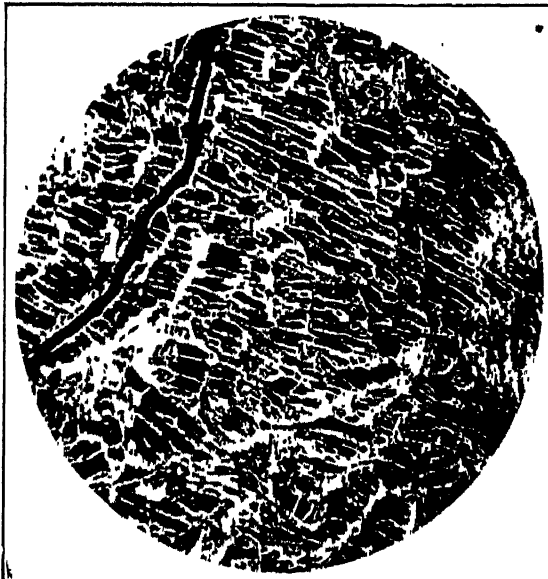


FIG. 2.—GRATING STRUCTURE FULLY DEVELOPED; PYRRHOTITE ENTIRELY REMOVED; MARY MINE.  $\times 36$ .



FIG. 3.—SPHEROIDS OF MARCASITE DEVELOPING IN FAIRLY FRESH PYRRHOTITE; ISABELLA MINE.  $\times 36$ .



FIG. 4.—THE SAME.  $\times 36$ .

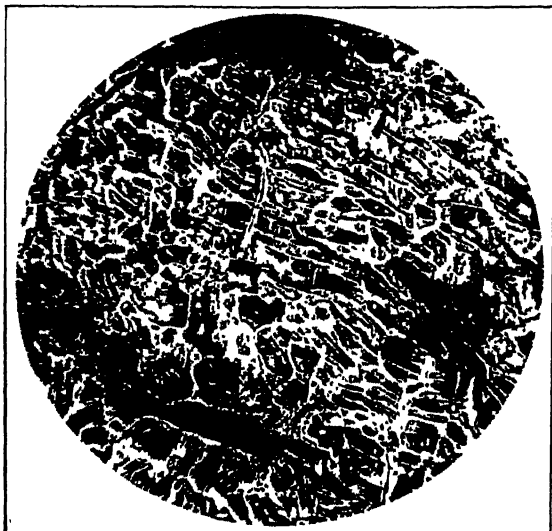


FIG. 5.—ENRICHMENT IN GRATINGS; THE SPACES BETWEEN MANY OF THE BARS ARE FILLED WITH CHALCOCITE-COVELLITE; MARY MINE.  $\times 36$ .

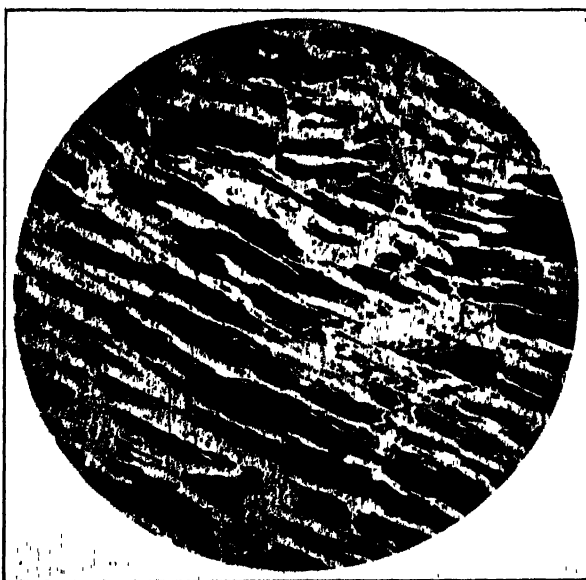


FIG. 6.—THE SAME.  $\times 100$ .





FIG. 7.—CHALCOCITE-COVELLITE REPLACING MARCASITE; EAST TENNESSEE MINE.  
× 100.

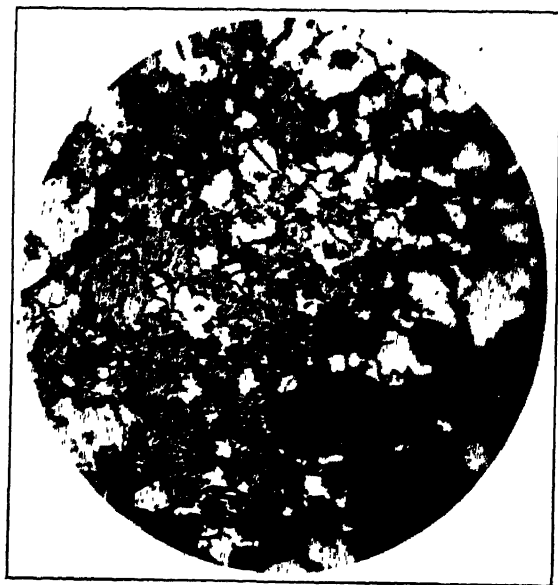


FIG. 8.—THE SAME. × 290.



FIG. 9.—SPHEROIDAL CHALCOCITE-COVELLITE IN CLAYEY GANGUE; BURRA BURRA MINE.  $\times 100$ .



FIG. 10.—CHALCOCITE-COVELLITE REPLACING GRAIN OF SPIALERITE, LEAVING RIM UNREPLACED; MARY MINE.  $\times 100$ .



FIG. 11.—CHALCOCITE-COVELLITE AND MARCASITE; MARY MINE.  $\times 290$ .



FIG. 12.—MARCASITE SPHEROIDS IN PYRRHOTITE; SUNSET MINE, ROSSLAND, B. C.  
 $\times 100$ .

but in these cases it is full of minute cracks and obviously undergoing attack of some sort.

The marcasite replaces pyrrhotite first and foremost, and in the early stages pyrrhotite is the only mineral attacked. Veinlets of marcasite can be seen traversing pyrrhotite and stopping abruptly at the border of a grain of chalcopyrite. Occasionally, they pass through sphalerite, but with diminished width. At a later stage, or when the action is more intense, there is no doubt that sphalerite is replaced by marcasite to an appreciable degree; some grains can be seen, under the high-power microscope, to be penetrated by groups of nearly parallel veinlets of marcasite giving a sort of horsetail effect. To sum up, marcasite replaces pyrrhotite very vigorously, sphalerite much more feebly, chalcopyrite and pyrite not at all.

Pyrrhotite, of course, differs from the other sulfides in the great ease with which it is dissolved by sulfuric acid; it is probably this fact that is responsible for its early alteration or removal from the zone of oxidation. Whatever the cause, the effect is beyond doubt; the pyrrhotite disappears altogether at a relatively early stage. The disappearance is almost absolute. Except for an occasional small grain sealed in by other more resistant minerals, the sulfide ore just below the gossan contains no pyrrhotite at all.

The other sulfides may be treated more briefly. Pyrite remains unaffected until a very late stage; only at the very contact with the gossan does it begin to alter. Solution cracks form in it, seeking out lines of weakness in the crystal and forming branching channels in it. In these cracks and around the margins, limonite begins to form. The crystals are broken up and the remainder of the decomposition is rapid.

Chalcopyrite is also rather resistant to the solutions; and long after the pyrrhotite has gone, the ragged grains of chalcopyrite remain scattered through the crumbling ore. There is remarkably little alteration in these grains; they seem to be almost as inert as the pyrite. In some of the specimens, it seemed possible that the chalcopyrite might be secondary; a few cases were noted where chalcopyrite surrounds and replaces a small core that appeared to be pyrrhotite in a way that has no parallel in the primary ore. However, most of the chalcopyrite in the near-surface material is certainly residual, for it contains inclusions of sphalerite and pyrrhotite, just like those in the primary ore, and it tends to be concentrated around pyrite crystals and around vugs (*i. e.*, around calcite) just as it is in the primary ore. Secondary chalcopyrite probably does occur, but it is of very minor importance.

Sphalerite is affected somewhat more than chalcopyrite but very much less than pyrrhotite, and residual grains are found until a fairly late stage. Magnetite is also comparatively resistant to oxidation and shows no sign of alteration to marcasite.

Of the gangue minerals, calcite is completely leached out early in the proceedings. At about the stage at which marcasite begins to become abundant, calcite disappears completely. The silicates are more resistant and often get into the gossan, while quartz is, of course, but little affected.

The net result of all this is a gradual crumbling. In a porphyritic ore of the Burra Burra type the phenocrysts of pyrite remain hard and bright, while the groundmass, through the disappearance of two of its most important components, pyrrhotite and calcite, goes to pieces. The pyrrhotite leaves behind a much smaller amount of marcasite, the calcite only vugs.

### *Enrichment*

The greater number of our polished sections showed no secondary copper sulfides at all, but one suite from a pocket in the Mary and several single specimens from other mines did contain appreciable amounts of chalcocite and covellite. These, with two specimens kindly furnished by Prof. J. F. Kemp, of Columbia University, and one from the Harvard museum, all collected a number of years ago, were sufficient to enable us to form a definite idea of the enrichment processes.

The secondary sulfide is, for the most part, not pure chalcocite. Firm chalcocite, white in polished sections, which is present in large amounts in many of the western mines, is conspicuously absent at Ducktown. There is a certain amount of pure covellite, but much more commonly the material is some shade of bluish white, and it can often be recognized under the high-power microscope as a mixture or intergrowth of chalcocite and covellite.

Some of the secondary sulfide is formed by the enrichment of sphalerite and chalcopyrite, especially of the former. In the specimens that show the greatest enrichment, the sphalerite is always replaced to a greater or less extent, and the enriching mineral is chiefly covellite. The chalcopyrite is affected very much less.

The black copper ores, however, were much too rich to be accounted for merely by the enrichment of the two minerals just mentioned. The pyrrhotite must, in some way, have played an important part. There must have been: (1) direct enrichment of pyrrhotite, (2) replacement of pyrrhotite and enrichment of the replacing mineral, or (3) enrichment by open space filling, *i. e.*, the precipitation in vugs (solution cavities) of copper sulfides by the reaction of copper sulfates with the hydrogen sulfide formed from the pyrrhotite. The first has not been demonstrated; on the contrary, it appears that the pyrrhotite is always removed before enrichment gets fairly started. The third is perhaps of some importance. To the writer, however, the second appears to be the critical reaction.

Most of the enrichment in our specimens is tied up with marcasite. The pyrrhotite alters to marcasite chiefly from grain borders and from

cleavage planes and other cracks, the result usually being a skeleton of marcasite with the interstices empty or filled with soft material. This interstitial material is, in many cases, enriched by chalcocite-covellite. There is some doubt as to just how these copper sulfides have formed. It is arguable that they may be precipitated by  $\text{H}_2\text{S}$  produced by the decomposing pyrrhotite; it is also conceivable that they may represent direct enrichment of rotten pyrrhotite; but the writer believes strongly that they are formed in the main by replacement of marcasite. As already stated, the texture of the marcasite varies a good deal. The material closest to the grain borders and cracks is hard, while farther in it is apt to be softer and spongy. This soft and spongy stuff, the intermediate stage in the transition from pyrrhotite to marcasite, would obviously be more easily affected by copper-bearing solutions than would the hard dense mineral. In more extreme cases, however, even the firmest marcasite is enriched vigorously. One of the richest of our specimens is composed of chalcocite-covellite with residues of marcasite, and it shows a spheroidal structure which appears to be inherited from the marcasite.

#### DISCUSSION

It seems, then, that the main requisite for a proper understanding of the processes, both of oxidation and enrichment, is a knowledge of the exact nature of the changes that take place in the pyrrhotite. It is strongly attacked and completely removed, and there is little doubt that the most active attacking agent is sulfuric acid. Sulfuric acid is generated in larger amounts during the oxidation of sulfides and hydrolysis of sulfates at the bottom of the gossan, and it is an effective solvent of pyrrhotite. The reaction is



That is to say, the iron goes into solution as ferrous sulfate, most of the sulfur is converted into hydrogen sulfide, and a small amount of sulfur (one-eighth, if pyrrhotite is taken as  $\text{Fe}_7\text{S}_8$ ) is left free. There is a further reaction possible here, one that has been recorded by Allen at the<sup>14</sup> Geophysical Laboratory. It is

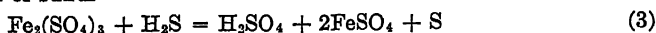


Here, then, is a possible explanation of the formation of some of the marcasite as an incident in the removal of the pyrrhotite. It is a reaction that can take place without the help of free oxygen, therefore well below water level, but it can fix only about one-seventh of the total iron. There is no doubt that locally, at least, a much greater proportion than this

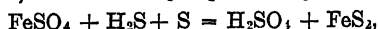
<sup>14</sup> E. T. Allen: Studies on Ore Deposition with Special Reference to the Sulfides of Iron. *Jnl. Wash. Acad. Sci.* (1911) 1, 6.

has been fixed as marcasite, and we must therefore look for some other reaction. This is not far to seek. Allen<sup>15</sup> says:

Experiments have, in fact, shown that both pyrite and marcasite may be obtained by the action of hydrogen sulfide on ferric-sulfate solutions. It is well known that ferric sulfate is directly reduced by hydrogen sulfide to ferrous sulfate with a simultaneous precipitation of sulfur

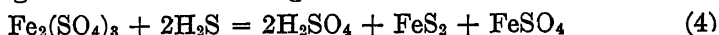


but it had not previously been noted that the further action of hydrogen sulfide and sulfur on ferrous sulfate slowly gives rise to a dark precipitate having the composition  $\text{FeS}_2$ . This reaction, which we may represent by the equation



takes place even at ordinary temperatures, though quite slowly. A microscopic examination of product proves that it is distinctly crystalline, though the crystals are minute. If the reaction is allowed to go on at a sufficiently high temperature, in a sealed glass tube, say 200° C., the crystals grow large enough to measure, and it has been found that they are partly marcasite—a mineral which has not previously been made artificially.

Combining reactions 3 and 2 we get



In this case one molecule of  $\text{Fe}_2(\text{SO}_4)_3$  would yield on solution by sulfuric acid  $7\text{H}_2\text{S}$ , which would produce  $3\frac{1}{2}$   $\text{FeS}_2$ ; in other words, one half of the iron could be fixed as marcasite.

The writer believes that it is this reaction which is mainly responsible for the formation of the marcasite. It is a matter of field observation that there is an almost unlimited quantity of ferric sulfate available; in fact, all or a great part of the iron passes through the ferric sulfate form as a normal step in its transition from sulfide to hydrate. It is, also, a matter of field observation that there is a great deal of sulfuric acid, and that hydrogen sulfide can often be smelled when the crumbling ore just under the gossan is broken into. Given these, the reaction would appear not only possible but inevitable.

The question has arisen whether the marcasite is formed by natural supergene processes at all, or whether it may not be merely a product of mine oxidation. It is true that many of the specimens we took came from places that had been exposed to the air for years. It is also true that stalactites of marcasite have been found growing on mine timbers. Nevertheless, the marcasite is so widespread, occurs in such large amounts, and appears to play so essential a part in the transition from primary ore to gossan, that the writer is unable to regard it as simply an accidental product of a few years' growth. If the hundred or more near-surface specimens he has examined are at all characteristic of the ore deposit as a whole, marcasite is one of the most important of the secondary minerals there. While not denying the probability that the reactions may have been locally accelerated by the opening of the pits,

<sup>15</sup> *Idem.* See also Allen, Crenshaw, Johnston, and Larsen: *Op. cit.*

the writer sees no reason why they should not have proceeded in the manner outlined above during the long period of secular oxidation. Given oxygen and water, the other steps follow logically—the manufacture of sulfuric acid, the attack on pyrrhotite with the formation of ferrous sulfate and hydrogen sulfide, the oxidation of the ferrous sulfate to ferric, the reduction of part of the ferric by more hydrogen sulfide with the formation of marcasite, and the breakdown of another part to limonite with the regeneration of sulfuric acid.

If this explanation is correct, the key to the whole situation is the abundance of hydrogen sulfide, which is the result of the action of strongly acid solutions on a very easily decomposed sulfide mineral. At the bottom of the gossan, just above the water level, oxidation is taking place, and sulfuric acid, ferric sulfate, and cupric sulfate are being manufactured. The water seeping into the primary ore below is, therefore, charged with these reagents. The sulfuric acid immediately attacks pyrrhotite, liberating hydrogen sulfide, which in turn reacts with ferric sulfate, reducing it and forming marcasite in practically the exact spot where the hydrogen sulfide is formed. Thus, by far the greater part of the marcasite replaces pyrrhotite, but a certain amount of hydrogen sulfide is also generated by sphalerite and therefore a minor amount of marcasite forms by replacement of that mineral.

The lower limit of the zone of alteration is sharp and close to the upper limit. Above the water level oxidation has done its work completely. Below the water level it is abruptly stopped for several reasons. One, and probably the important one, is the fact that the vadose solutions are diluted, on reaching the water level, to such an extent that they lose nearly all their potency. Another is the physical nature of the ore—its compactness and impermeability. A third is the fact that the breakdown of the pyrrhotite and removal of calcite cause a great increase in the porosity of the topmost layers of the sulfides, so that they present a large surface area to the attacking solutions and tend to neutralize them before they can penetrate far into the primary ore. Hence, instead of oxidation and enrichment proceeding in two definite zones, one above the other, they are very much telescoped. This may explain why ferric sulfate, which belongs in the oxidizing zone, can succeed in getting down to the primary ore before enrichment begins, as some of it must do if it is in fact the source of the iron in the marcasite. It cannot have done so in excessive amounts, for chalcocite was formed later than part of the marcasite and chalcocite is unstable in the presence of ferric sulfate. However, the marcasite reaction, as already indicated, is a two-stage process. There is first the reduction of ferric sulfate to ferrous by  $H_2S$  with the liberation of sulfur, and second the reaction of the ferrous sulfate and free sulfur with more  $H_2S$  to form marcasite. If the acidity is high and the reaction with pyrrhotite rapid, there is probably enough  $H_2S$



generated to take care of most of the ferric sulfate and prevent it from attaining any very high concentration in the chalcocite zone. Further, the sulfur used in the earliest formed marcasite may be largely the excess sulfur of the pyrrhotite itself and not derived from ferric sulfate at all.

It seems necessary, nevertheless, to conclude that the secondary copper has precipitated in the presence of some ferric sulfate; in this connection it is interesting to note that the copper mineral is largely covellite, or at least a chalcocite-covellite intergrowth. Covellite is much more stable than chalcocite with respect to ferric sulfate.

The effect of sulfuric acid is to retard the enrichment of chalcopyrite and accelerate that of sphalerite.<sup>16</sup> In the case of sphalerite, high acidity tends to produce covellite rather than chalcocite.<sup>17</sup> In most deposits, chalcopyrite enriches more readily than sphalerite, and chalcocite is a more common enrichment product than covellite, but the observed facts at Ducktown are that sphalerite enriches to a far greater extent than chalcopyrite and that its enrichment product is chiefly covellite. This confirms the conclusion that the solutions were rather strongly acid.

The strict coincidence of the zone of enrichment with the water level has already been explained by the supposition that oxidation has been able to remove completely all sulfides above that level. The history of the deposits is conceived to be as follows: The orebodies were formed after the main period of regional metamorphism but while the present surface was still buried to a depth of several thousand feet; that is, they were formed at or soon after the end of the Appalachian revolution, say, in late Permian or early Mesozoic times. Mesozoic erosion brought them to the surface, and the country was reduced to old age in about the Cretaceous period. At or before this time, therefore, oxidation was able to outdistance erosion and reach the water level, where it was stopped abruptly by dilution of the solutions and a dearth of oxygen. The condition attained at that time has persisted to the present day, for there has since been only a moderate amount of uplift and dissection, and the zone has easily adjusted itself to the changes in the water level.

#### OTHER OCCURRENCES OF MARCASITE AFTER PYRRHOTITE

##### *Gossan Lead, Virginia*

Immediately after visiting Ducktown, the writer spent a day at the Gossan mine, at Monarat, Va. This is on the Gossan Lead, a belt of pyrrhotite ore running for many miles through southwestern Virginia. In their mineralogy, geologic relations, and climatic conditions, these

<sup>16</sup> Zies, Allen, and Merwin: Secondary Copper Sulphide Enrichment. *Econ. Geol.* (1918) 11, 502.

<sup>17</sup> Zies, Allen and Merwin: *Op. cit.*, 491.

deposits bear a rather strong resemblance to those of Ducktown. The primary ore contains less copper, the topography is more rugged, and erosion probably more rapid, but, on the whole, the phenomena of oxidation are very like those of Ducktown. A suite of specimens collected in the open pits at the top of the sulfide ore showed an exactly similar development of marcasite, both in spheroids and with grating structure.

*Rossland, B. C.*

This is another camp in which pyrrhotite is the chief sulfide, but there is no deep oxidation like that at Ducktown and the Gossan Lead. Nevertheless, two specimens picked up by the writer on the dump of the Sunset mine, a prospect in the "south belt" of the camp, showed in polished section a small but unmistakable development of marcasite in the pyrrhotite as veinlets and small spheroids. In these specimens, the marcasite is associated with limonite, which was not the case in the fresher specimens from Ducktown. It is suggested that the reason may be that oxidation is proceeding at a much slower rate, the concentration of sulfuric acid is much smaller, and the attack on pyrrhotite much milder. The ferric sulfate is partly reduced to marcasite, but the consumption of acid allows part of it to hydrolyze to limonite.

Beginnings of the marcasite alteration were detected in a specimen from the pyrrhotite-nickel deposit at Dracut, Mass. On the other hand, a few specimens from the glaciated outcrops of the Sudbury orebodies showed no sign of marcasite, the pyrrhotite apparently oxidizing directly to limonite.

It seems probable that marcasite will be found to be quite a common product of pyrrhotite alteration, especially where conditions are favorable for the production of a strong concentration of sulfuric acid in the zone of oxidation.

SUMMARY AND CONCLUSIONS

1. The key to both oxidation and enrichment at Ducktown is the behavior of the pyrrhotite, which is easily soluble in sulfuric acid with evolution of hydrogen sulfide.

2. The pyrrhotite is in part dissolved, in part replaced by marcasite. The formation of marcasite is believed to be due mainly to the reaction of hydrogen sulfide with ferric sulfate.

3. This change commences before the period of enrichment, and enrichment takes place chiefly at the expense of the marcasite.

4. The secondary copper sulfides are chalcocite and covellite. The relative abundance of covellite is believed to be due to the high acidity of the enriching solutions, and to some extent to the presence of ferric sulfate.

5. The enrichment of sphalerite is important; sphalerite is affected to a much greater extent than chalcopyrite.

6. Chalcopyrite is rather inert to enrichment; secondary chalcopyrite occurs only in minor amounts.

7. The position and shape of the zone of enrichment are accounted for as follows: During the period of peneplanation oxidation was able to remove all sulfides above the water level, and it has been able to keep pace with the moderate changes in the water level due to subsequent dissection. It has been unable to work effectively for more than a very few feet below the water level because of dilution of the solutions and the imperviousness of the ore.

#### ACKNOWLEDGMENTS

The writer is indebted to Prof. L. C. Graton, who directed the field work and has followed the developments of the microscopical study. The thanks of both are due to the officers of the Tennessee Copper Co. and the Ducktown Sulphur, Copper, and Iron Co. and especially to Messrs. H. B. Henegar, Russell Johnson, W. Y. Westervelt, and J. H. Taylor, for much information and kind assistance in the field work. The writer is also indebted to Mr. Edward I. Williams, superintendent of the Gossan mine, for his hospitality and help.

#### DISCUSSION

A. C. LAWSON, Washington, D. C.—The author spoke of two classes of deposits—one with an abundance of iron sulfide and one with a scant amount of iron sulfide. Is there any difference in the gossan in those two cases?

The author referred to the zone of enrichment as being a foot or two; is not that a very limited depth of enrichment? It occurs to me that if the ground water were stagnant, the reducing quality of that water would tend to be exhausted as the process went on, and there would be a shallow depth of enrichment; but if the water were circulating the reducing qualities of the water would be maintained and so favor a deeper zone of enrichment. At Ely, the gossans of two deposits in the same general porphyry are very different. At Ruth, the gossan contains nothing but limonite; there is no carbonate in it; it is over a mile away from Copper Flat. At Copper Flat, before the pit was dug and concealed the evidence, the porphyry was full of carbonates, malachite, and azurite; a totally different type of gossan. It has been suggested that in one case there was much pyrite and in the other the pyrite was scant, and that any acid due to oxidation was neutralized by limestone.

A. C. SPENCER, Washington, D. C.—The author stated that undoubtedly these solutions were acid. It is not apparent to me where the

acidity arises in ferrosulfate, which I think would give us merely ferrous sulfate by the first oxidation and not ferrous sulfate plus sulfuric acid, as would be the case if it were pyrite.

GEOFFREY GILBERT.—In both cases the original ore is practically all iron sulfide. You can get all the acid you want from the hydrolysis of ferric sulfate. Just exactly what the reactions are that occur, I could not say offhand.

JAMES F. KEMP, New York, N. Y.—All the mines have abundant pyrrhotite, but one of them, the Burra Burra, has a good deal of pyrite replacing the pyrrhotite.

AUGUSTUS LOCKE, San Francisco, Calif.—In the ordinary gossan, the acid is likely to be used up by combination with the bases of the rock; in this gossan, the amount so used up is probably less than is usual. The calcite, of course, must use up its amount of acid, but together with the other minerals it is not abundant enough to *kill* the acid as it is *killed* in many gossans and in most of the cappings of the disseminated deposits.

JAMES F. KEMP.—There is one other possible explanation or a factor that may enter into the explanation of the narrow gossan. I spent some time in Ducktown, 20 or 25 years ago, before the Tennessee Copper Co. started its great operations and before many of these veins were opened to the extent they are now. It was possible to go into the old tunnels and follow out the old water-line whence the early miners had taken the black ores. There were "floors," as the local miners called them, of quartz associated apparently with some of the black ores, and it was a rather common phrase in the camp then, that the black ores had gathered on these cross veins or so-called floors of quartz. I saw some solid tabular masses of quartz transverse to the vein and apparently right under the horizon where the black ores were found.

GEOFFREY GILBERT.—Henrich featured those in his account of Ducktown. We did not see anything corresponding to them at all though we got into a lot of the very old workings.

SHERMAN F. KELLY, Toronto, Ont.—The author states that chalcopyrite is rather inert to enrichment, which is rather unusual; is there any special explanation for it at this camp?

GEOFFREY GILBERT.—The explanation I have advanced in this paper was the high acidity of the solutions; sphalerite enriches best when solutions are acid.

J. T. SINGEWALD, Baltimore, Md.—If this reaction takes place in pyrrhotite, why does not it also take place in an ore composed almost entirely of pyrite?

GEOFFREY GILBERT.—The pyrrhotite is much more soluble than pyrite in sulfuric acid and consequently generates much more hydrogen sulfide.

L. C. GRATON, Cambridge, Mass.—I presume that the water which has stood for countless thousands of years saturating a sulfide ore is reducing in its nature. That reducing power may be considerably more available than the reducing power of the sulfide ore that originated it; but in relative quantities, the reducing power in the water is infinitesimal compared with the reducing power in the ore. Until atmospheric gaseous oxygen gets into that ore and increases its permeability, you have a strongly reducing environment in the ore itself. I fancy the ground waters saturating the sulfide ore were essentially stagnant. They were transporting chemical material, however, at as rapid a rate as they could by diffusion, but because of the relatively great quantity of water in the essentially neutral ground water, in proportion to the small quantity of active reagents that were fed to the ground water from the oxidized zone, the degree of dilution of the latter was too great to permit essential modification of the sulfide ore more than a few feet below the water level.

This Ducktown example is relatively unique, in two or three respects. In all the camps we have studied, this was the first example in which we have found any evidence of a secondary iron sulfide having been deposited. We have found no secondary pyrite deposited in the secondary enrichments whatever. There have been a few cases where marcasite occurs in doubtful relations which, so far as I know, none of us has been able to resolve. But here is a case of secondary marcasite on an important scale, and presumably the reason for it is the pyrrhotite. I suppose, however, that pyrrhotite would likewise have formed in Ducktown on a considerable scale if the water level had been definitely below where it was and is. In other words, I do not believe it is the water level that essentially controls the presence of the secondary marcasite. Marcasite was determined by an unusually high acid concentration, partly because of the great quantity of sulfur in the original ore, acting on so easily decomposable a mineral as pyrrhotite, which not only is easily soluble but yields great quantities of hydrogen sulfide in the course of its solution.

AUGUSTUS LOCKE, San Francisco, Calif.—One of the things that has interested me is the thin tabular enrichment. It is quite easy to accept the conclusion that the enrichment is thin and tabular because the drop of water going down from the surface, so long as it is in the gossan, finds a very permeable material to pass through, and continues to find a permeable material so long as it is in the sandy sulfide that has been affected by oxidation; but when it suddenly encounters the unaltered sulfide, a very impermeable material, its path instead of having a very large vertical component, tends to have a very large horizontal component. In

all the ores at which I have looked, and which continue to be permeable below the top of the sulfides, there is a tendency for secondary enrichment, if it occurs at all, to continue downward a long way.

As to the silica floors mentioned—is there any possibility that they are residual concentrations of the silica contents of the ore during oxidation? Do they represent a certain thickness of ore from which all the iron oxide has been leached out without the corresponding deposition of iron oxide? I am thinking of conditions such as those existing in the Kyshtim deposits in the Urals which show residual sands greatly enriched in gold and silver, but from which the iron, copper and the other soluble things are practically all gone.

One is inclined always to expect supergene chalcocite to be a replacement of another sulfide; that is a general rule in the Western deposits. Here, however, we have a very good source of abundant hydrogen sulfide, so the question at once arises, is not a good deal of the chalcocite what might be called an *open-space filling*? That is, not a replacement of another sulfide, but a deposition in non-sulfide gangue or a deposition in open spaces? I understand that point is somewhat discussed here and the conclusion is that not a very large proportion is of that kind, but I think we should put Ducktown, because of its hydrogen sulfide complications, in a separate class from most of the deposits in which we have worked; we should expect to get all kinds of effects unknown in a place, for example, like Ely.

JAMES F. KEMP.—We must be cautious in our expectations coming from the semi-arid or arid regions of the West with deep-down ground water to the abundant rainfall and ground water of the East. I thought in my trip years ago, that the ground water standing there protected the underlying pyrrhotite from further change, as it generally does. The diffusion of sulfides through its agency appealed to me as an exceedingly slow process, and one limited to short distances.

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## Magnetite Deposits of Eastern Porto Rico

BY CHARLES R. FETTER,\* PH.D., PITTSBURGH, PA.

(New York Meeting, February, 1924)

IN CONNECTION with the gathering of data for a report on the geology of the Humacao district of southeastern Porto Rico during the summer of 1916, under the auspices of the Scientific Survey of Porto Rico and the Virgin Islands, conducted by the New York Academy of Sciences, the writer had an opportunity to make a brief examination of the magnetite deposits of the eastern portion of the island. Inasmuch as these deposits have attracted some attention as possible future sources of iron ore, and as there is only scanty reference made to them in literature,<sup>1</sup> a short description based on this reconnaissance survey was deemed to be worthy of record.

The magnetite deposits of eastern Porto Rico occur in association with a belt of limestone, trending approximately S 53° E, which begins 1½ miles east of Juncos and can be traced for about 6 miles toward the coast. Four outcrops of magnetite were observed, which are designated as Nos. 1, 2, 3, and 4, respectively, on the map shown in Fig. 1. Others are probably present, but escaped notice on account of the thick mantle

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<sup>1</sup> Charles P. Berkey: Geological Reconnaissance of Porto Rico. *Ann. N. Y. Acad. of Sci.* (1915) 26, 55.

Manuel Victor Domenech: Porto Rico, Her Mineral Resources—Their Value and the Reasons Why They Are Not More Developed. *Mines & Minerals* (1899) 19, 531.

Harbert S. Hamilton: Notes on Some Ore Deposits of Porto Rico. *Eng. & Min. Jnl.* (1909) 88, 518.

Robert T. Hill: "Cuba and Porto Rico with the Other Islands of the West Indies," 150 and 421. New York, 1899.

H. B. C. Nitze: Investigations of Some of the Mineral Resources of Porto Rico. 20th *Ann. Rep. of U. S. Geol. Surv.* (1899), Part VI (continued) 786.

William F. Willoughby: Mineral Industries of Porto Rico. Special Reports, Mines and Quarries (1902), Bur. of Census (1905) 1077. Quoting from Second Annual Report of Governor of Porto Rico to President of United States.

of residual soil, which in most places conceals the bed-rock formations. One deposit,  $\frac{9}{10}$  mile south of Torres, designated as No. 5, lies about  $\frac{3}{10}$  mile northeast of the main belt.

The outcrop east of Juncos, No. 1, is the most prominent and this deposit is probably the largest of those examined. Inasmuch as there are no fuels available in Porto Rico for the establishment of a local iron industry, the ores, if exploited, will have to be shipped. The two nearest harbors at which shipping facilities are at present available are San Juan and Fajardo Playa; of these, San Juan is by far the better. By way of the Gurabo and Rio Grande de Loiza valleys, the Juncos deposit is 31 miles distant from San Juan. The electric and narrow-gage steam railroad from San Juan to Caguas covers the distance to the mouth of the Gurabo River; thence it is 10 miles up the Gurabo valley to the magnetite deposit. For most of this distance a light narrow-gage track has been constructed for the transportation of sugar cane from the fields to the central "Juncos."

By way of the headwaters of the Gurabo River, across the divide to the Rio Blanco valley, down this to Naguabo, thence parallel to the coast to Fajardo Playa, the distance is about 27 miles. Ensenada Honda, south of Fajardo Harbor, is 7 miles nearer but has no shipping facilities. Along all but the first 9 miles of this distance, light narrow-gage tracks are already laid for the hauling of cane. The only steep grades along this route occur after leaving the headwaters of the Gurabo River and going down Pena Pobre Creek, a tributary of the Rio Blanco. Along this the haul would be down-grade.

The deposits are, probably, not of sufficient size to warrant the expenditure of large sums of money for transportation facilities, therefore such facilities as are available would have to be used to exploit the deposits at a profit.

#### OUTLINE OF GEOLOGY OF DISTRICT

The interpretation of the bed-rock geology of the area under consideration is difficult because of the thick mantle of residual soil over most of it. In the lowland regions, outcrops are few; and those that do occur are usually considerably decomposed. Formational boundary lines, therefore, can be traced only approximately. The best exposures are found along stream beds and recent road cuts and occasionally at or near the crests of the ridges. The formations have been folded and invaded by numerous intrusives but reliable strike and dip measurements can rarely be obtained on account of the massive character of most of the rocks involved and the scarcity of outcrops.

The oldest formations exposed belong to what Berkey has called the "older series,"<sup>2</sup> their distribution is shown in Fig. 1. They prob-

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<sup>2</sup> Charles P. Berkey: *Loc. cit.*, 10.



ably represent some of the lowermost members of the series. Berkey considers the whole series to be of Cretaceous age, using the term to include both the Upper Cretaceous and Lower or Comanchian.<sup>3</sup> Later workers in other parts of Porto Rico concur with him pretty well in this

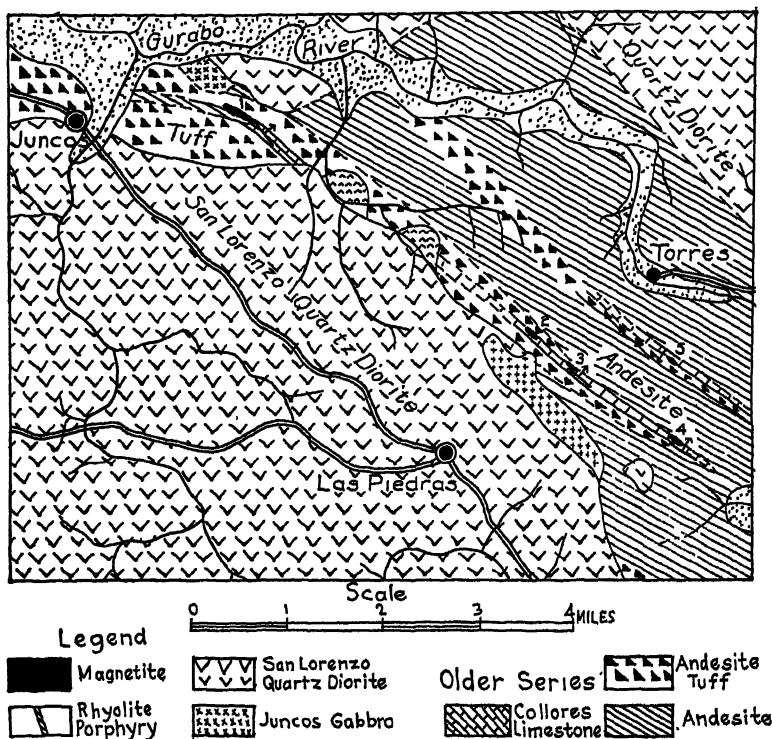


FIG. 1.—GEOLOGIC MAP OF JUNCOS-TORRES DISTRICT.

correlation.<sup>4</sup> In the area under investigation, the writer was not able to find any fossils.

In the Juncos-Torres region, the "older series" consists chiefly of andesites, andesite tuffs, and limestone; the andesites predominate. They show a rather wide range in texture and mineralogical composition and include some dacites and latites. Augite and hornblende

<sup>3</sup> Charles P. Berkey: *Loc. cit.*, 58.

<sup>4</sup> D. R. Semmes: *Geology of San Juan District*. "Scientific Survey of Porto Rico and the Virgin Islands," N. Y. Acad. Sci. (1919) 1, I, 72.

E. T. Hodge: *Geology of the Coama-Guayama District*. *Idem.* (1920) 1, II, 192.

G. J. Mitchell: *Geology of the Ponce District*. *Idem.* (1922) 1, III, 285.

Bela Hubbard: *The Geology of the Lares District*. *Idem.* (1923) 2, I, 34.

varieties are of most frequent occurrence and a porphyritic texture is usually developed in them. Both extrusive and intrusive types are undoubtedly represented, but it is difficult to differentiate these in the field. In many instances, a parallel alignment of the plagioclase laths of the groundmass, indicating a flowage structure, is revealed under the microscope.

The tuffs rank next to the andesites in order of abundance. They are predominately andesitic in composition, but latite varieties are present. In texture, some of them are sufficiently coarse to be classed as volcanic breccias. Others contain sufficient calcareous material to be classified as calcareous tuffs; sometimes, these grade into tuffaceous limestone. In the vicinity of the magnetite deposits, the tuffs have frequently been metamorphosed into hornblende schists; similar changes have taken place along their contacts with the major intrusive of eastern Porto Rico, the San Lorenzo batholith.

Limestones, while the least abundant of the three types of rocks comprising the "older series," are the most important in the Juncos-Torres district on account of the intimate association of the magnetite deposits with them. Their outcrops occur along two belts; one begins  $1\frac{1}{2}$  miles east of Juncos and extends S  $53^{\circ}$  E for about 6 miles; it has been called the Collores limestone because of its typical development in the barrio of Collores de Piedras, northeast of Las Piedras. The dip is toward the northeast and ranges from  $32^{\circ}$  to  $41^{\circ}$ . The second belt was traced for only a short distance. It lies about  $\frac{1}{10}$  mile northeast of the southeast end of the first and apparently dips toward the southwest, although the character of its outcrop makes it impossible to determine this positively. This makes it appear that a syncline is present and that the two belts may be formed by outcrops of the same bed.

Along the southwest belt, the best development of the limestone appears in the vicinity of outcrop No. 3 in the barrio of Collores de Piedras. The limestone has a strike of N  $54^{\circ}$  W and dips  $32^{\circ}$  toward the northeast. Prominent ledges of gray and white crystalline limestone, in some instances 40 ft. thick, crop out; the total thickness is estimated to be 250 ft. Qualitative analyses indicate a very pure limestone. There is very little residue after treatment with cold dilute hydrochloric acid and only slight amounts of iron and alumina and a trace of magnesium carbonate are present. In the vicinity of the magnetite occurrence, the limestone has been converted into an aggregate of calcite, garnet, pyroxene, chlorite, quartz, magnetite, and specular hematite. Garnet is the most abundant of the metamorphic minerals.

At the northwest end of the belt, just southeast of the Juncos magnetite deposit, the limestone has been completely metamorphosed into an aggregate of garnet, pyroxene, amphibole, epidote, chlorite, and talc. Only minor amounts of calcite are still present in it. At the southeast

end, 1500 ft. northwest of outcrop No. 4, prominent ledges of white crystalline limestone can also be seen. Some garnet rock is associated with them.

Along the northeast belt, outcrops of limestone were observed at only one locality, about  $\frac{9}{10}$  mile south of Torres. It is a dark gray, fine-grained variety that has not been metamorphosed to the same extent as the limestone of the first belt. An examination of thin sections shows that it consists principally of calcite; but occasional grains of quartz, augite, and plagioclase are present. The latter undoubtedly represent tuffaceous material deposited simultaneously with the calcareous constituents. A few small grains of pyrite are also present. Southeast of this limestone, along the strike, a prominent ledge of metamorphosed rock was noticed in one place; under the microscope, this was found to consist almost entirely of an aggregate of vesuvianite grains. A little pale green amphibole and deep brown biotite occur between the former. This rock apparently represents metamorphosed portions of the limestone. At outcrop No. 5, only one place was discovered where a strike and dip determination could be made. The former was found to be N 48° W and the latter 52° toward the southwest. The determination was taken on a prominent ledge of andesite, showing indications of a flowage structure under the microscope, which rests upon the limestone.

The San Lorenzo batholith, a great intrusive mass of quartz diorite, lies a short distance to the southwest of the major limestone belt. Its contact with the "older series" runs nearly parallel to the limestone outcrop. The Luquillo stock, composed of a similar intrusive rock, which is undoubtedly an offshoot of the former, bounds the "older series" on the north and northeast. The San Lorenzo batholith has produced pronounced contact metamorphic changes in the tuffs of the "older series" in many places where it has come into contact with them. In some instances, all traces of original structures have been obliterated with the conversion into hornblende schists.

Under the microscope, the San Lorenzo quartz diorite is seen to be composed principally of plagioclase feldspar of the andesine or acid labradorite variety, quartz, and a dark brownish green hornblende. Orthoclase, biotite, occasionally augite, magnetite, titanite, and apatite are the chief accessory constituents. The rock, as a rule, possesses a coarse granitoid texture. This phase is, by far, the predominating type but sometimes quartz drops out almost entirely so that the rock becomes a diorite; in a few other instances, orthoclase takes the place of plagioclase, producing a hornblende granite, and in rare cases augite replaces hornblende, so that the rock is augite diorite. Occasionally, in the case of the smaller offshoots, the texture is porphyritic.

With the exception of the andesite porphyries of the "older series," some of which are undoubtedly intrusive, only one small intrusive mass

was found in this area older than the San Lorenzo quartz diorite. This is immediately northwest of the Juncos deposit; it possesses a granitoid texture and has the mineral composition of a gabbro. The microscope shows it to consist chiefly of plagioclase feldspar of the labradorite variety and augite. A little greenish brown hornblende occasionally occurs as reaction rims around the augite. Titanite is the chief accessory constituent. Small tongues of quartz diorite projecting into the gabbro along its contact with the latter clearly indicate that the Juncos gabbro is the older rock.

Southwest of outcrops Nos. 2 and 3, an intrusive mass of coarse light pink granite lies between the "older series" and the San Lorenzo batholith. This has been called the Yabucoa granite on account of its typical development in the vicinity of Yabucoa Playa, where it is intrusive in the quartz diorite. The rock possesses a coarse granitoid, in some instances almost pegmatitic, texture. Under the microscope, the two chief constituents are found to be orthoclase and quartz; only minor amounts of plagioclase and a little biotite occur in it.

Two other small intrusive masses, also situated along the contact between the quartz diorite and the "older series" between outcrops Nos. 1 and 2, are worthy of mention. Thin sections show that they possess a porphyritic texture with the phenocrysts in excess. The predominating minerals are plagioclase, orthoclase, and a dark greenish brown hornblende. The groundmass is made up largely of feldspar and quartz occurring in part as micrographic intergrowths. Magnetite, apatite, and titanite are the principal accessory constituents present. These intrusives are correlated with the Patillas quartz monzonite, which was intrusive in the Yabucoa granite southeast of the town of Patillas along the southeast coast of Porto Rico.

Aplite, granite, rhyolite, trachyte, dacite, and andesite porphyry dikes cut not only the "older series" but also the San Lorenzo quartz diorite and the Yabucoa granite. All of these intrusives have been shown, by other workers on Porto Rican geology, to be older than the oldest of the Tertiary beds that overlie the "older series" unconformably along the north and south coasts of the island, as they are nowhere found to intersect them. The lowermost members of the Tertiary series are Middle Oligocene.\*

#### DESCRIPTION OF MAGNETITE DEPOSITS

##### *Deposit at Outcrop No. 1*

The magnetite deposit at outcrop No. 1 lies  $1\frac{1}{2}$  miles east of Juncos along the crest of a ridge, south of the Gurabo valley, that rises approximately 375 ft. above the lowlands to the north and south. The map,

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\* Bela Hubbard: *Loc. cit.*, 65.

Fig. 2, based on field notes, shows the relationship of the outcrop to the surrounding formations; Fig. 3 shows the ridge, looking toward the north.

The outcrop has a strike of  $N\ 60^{\circ}\ W$  and apparently dips  $62^{\circ}$  toward the northeast. It can be traced for 2000 ft. along the crest of the ridge, but the best development of magnetite occurs at the northwest end, where

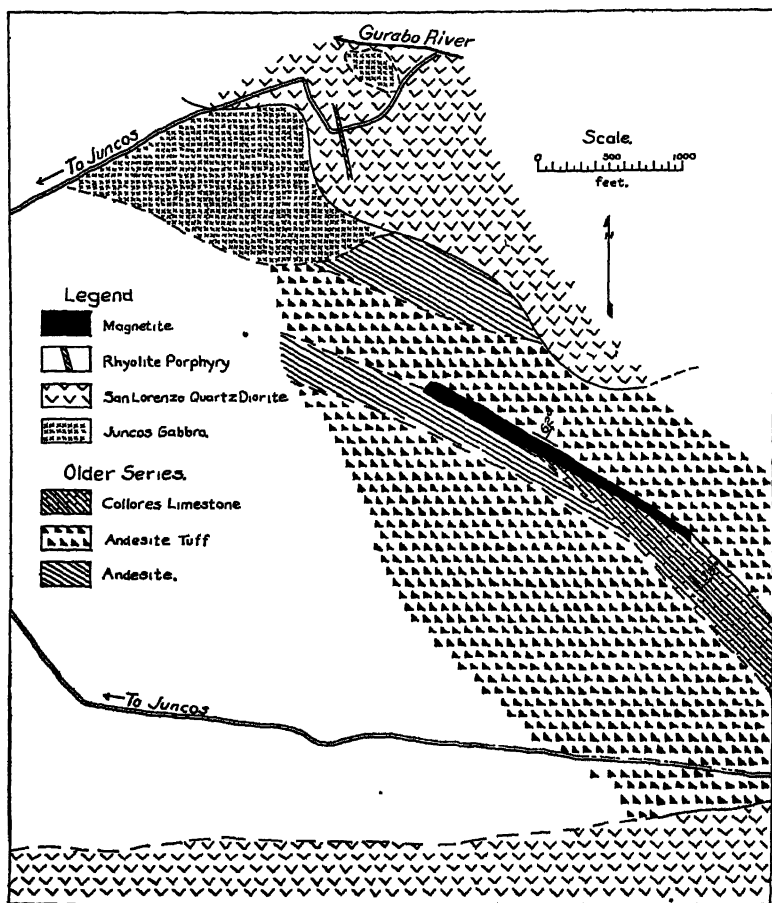


FIG. 2.—RELATIONSHIP OF OUTCROP NO. 1 TO SURROUNDING FORMATIONS.

large boulders and prominent ledges of nearly pure magnetite are very conspicuous. Much of the magnetite in the outcrop at the northwest end is fine-grained and nearly pure. It possesses a porous structure, due undoubtedly to the leaching out of silicates and perhaps small amounts of sulfides by weathering. Octahedral crystals of magnetite sometimes line drusy cavities. Part of the magnetite is sufficiently magnetic to pick up small tacks. Occasionally a fine-grained inter-

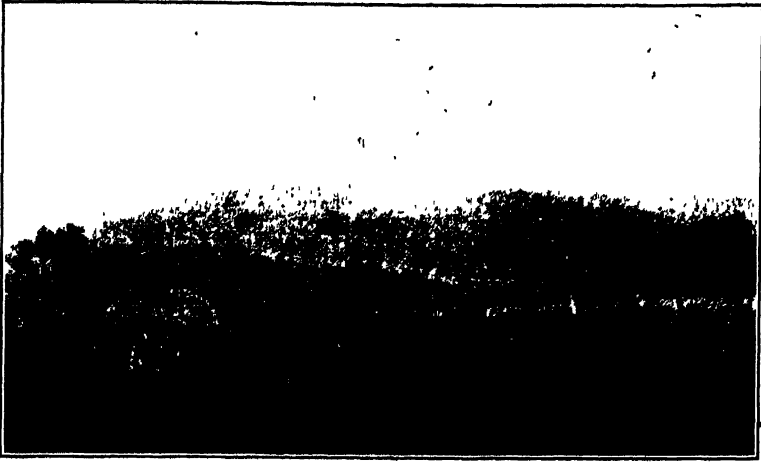


FIG. 3.—RIDGE WITH MAGNETITE DEPOSIT EAST OF JUNCOS.

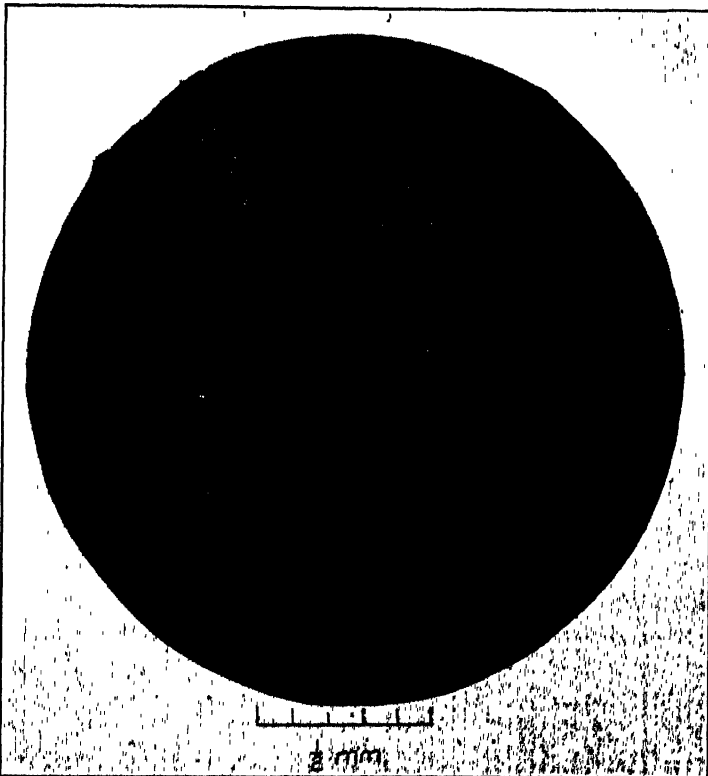


FIG. 4.—MAGNETITE ORE FROM WESTERN END OF JUNCOS DEPOSIT; BLACK MINERAL IS MAGNETITE, LIGHT MINERAL IS GARNET.

growth of magnetite and specular hematite occurs; qualitative analyses show only traces of titanium. In several places a little malachite was noticed; this is presumably derived from a sulfide, such as chalcopyrite, and indicates that, in depth, small amounts of sulfides are probably present in association with the magnetite. Garnet occurs with the magnetite at the west end of the deposit; under the microscope, it shows pronounced optical anomalies and complex twinning. A little fibrous amphibole has been formed from it by alteration. At the east end, the



FIG. 5.—MAGNETITE ORE FROM EASTERN END OF JUNCOS DEPOSIT; BLACK MINERAL IS MAGNETITE, LIGHT MINERAL IS EPIDOTE.

magnetite occurs with much larger amounts of silicates. A thin section of a specimen shows epidote to be the predominating mineral with which the magnetite is associated, but small patches of garnet are also present; Fig. 4 shows the association of magnetite and garnet, and Fig. 5 that of magnetite and epidote.

Toward the southeast, the magnetite is succeeded by a belt of metamorphic rock, which is thought to have been derived from the Collores limestone, perhaps a tuffaceous phase. Numerous prominent ledges crop out along the hillside. At one place, about 400 ft. beyond the

orebody, the strike is N 37° W and the dip 38° NE. Large vugs occur in the metamorphosed rock in places. A microscopic examination reveals that the rock is largely pyroxene and garnet, the garnet having developed after the pyroxene; calcite, epidote, quartz, and talc are present in minor amounts and chlorite has developed along minute fractures. Another specimen taken from the walls of one of the vugs consists largely of garnet and amphibole with some talc; the garnet apparently formed first, then the amphibole, and finally the talc.

Hornblende and pyroxene schists, undoubtedly derived from andesite tuffs, overlie and underlie the metamorphosed limestone. A thin section of a specimen obtained from above the limestone possesses a distinctly foliated structure. It is made up chiefly of plagioclase, quartz, orthoclase, and a deep green hornblende; a little pyroxene is also present. The outlines of a few original feldspar crystals now completely altered to kaolin, sericite, and epidote can still be recognized. Magnetite and titanite are present as minor constituents. A specimen taken from a point some distance below the limestone also possesses a schistose appearance. It is composed of an interlocking mosaic of pale green pyroxene, plagioclase, orthoclase, and a little dark green hornblende. A few large crystals of pyroxene full of inclusions, of which some are smaller pyroxene grains, are present; magnetite occurs in minor amounts and epidote has developed along minute fractures.

At the west end, an augite andesite occurs as the foot wall of the magnetite deposit. It possesses a felsitic texture with a tendency for the many feldspar laths of the groundmass to be in parallel alignment, indicating a flowage structure. A few phenocrysts of plagioclase of an andesine or acid labradorite variety and a little augite are present. The matrix consists chiefly of plagioclase. Titanite is an accessory mineral. Pale green hornblende aggregates occur along small fractures as well as in places once occupied by augite phenocrysts. The plagioclase is clouded by alteration products.

In one place north of the deposit, an outcrop of metamorphosed andesite tuff was observed. It shows a fine texture and a slight tendency toward a schistose structure. Grains of augite, plagioclase, and orthoclase up to 0.4 mm. in length are present. The matrix consists chiefly of an allotriomorphic intergrowth of quartz and pale green hornblende. A little chlorite has developed from hornblende.

Beyond the andesite tuff, toward the northwest, there is an occurrence of hornblende andesite porphyry. Augite phenocrysts with reaction rims of hornblende are prominent. The matrix is, predominately, a brownish green hornblende with only minor amounts of plagioclase; it is coarse in texture. A little magnetite and apatite are present.

The Juncos deposit lies about 2500 ft. north of the San Lorenzo quartz diorite batholith. An offshoot of the latter, which may be part of the Luquillo stock, crops out 500 ft. north of the magnetite occurrence.



*Deposit at Outcrop No. 2*

The magnetite deposit at outcrop No. 2 is situated about  $3\frac{3}{4}$  miles southeast of outcrop No. 1 on the south side of a ridge about 160 ft. below its crest and 365 ft. above the valley at its base. The outcrop strikes N  $50^{\circ}$  W and can be traced for 335 ft. The dip appears to be  $72^{\circ}$  toward the northeast.

Magnetite is the chief ore mineral present but some fine-grained specular hematite occurs. Garnet is the predominating gangue mineral appearing in the outcrop. Drusy cavities lined with trapezohedrons of garnet and sometimes small octahedrons of magnetite, as well as crystals of quartz, are common. Veinlets of magnetite and quartz cut massive garnet rock; the garnet is reddish brown. A qualitative analysis indicates that it is the andradite variety, silica, iron oxide, and lime being the chief constituents. Alumina occurs in only small amounts and magnesia is absent.

A green brecciated rock forms the north, or hanging, wall of the deposit; the dark green portion is intersected in all directions by streaks of light-colored material. Under the microscope, the dark green portions are found to consist chiefly of pyroxene associated with small amounts of garnet. The light portions represent an allotriomorphic intergrowth of plagioclase, orthoclase, quartz, and some pyroxene. It is thought that this rock represents a metamorphosed andesite tuff, probably a calcareous one.

North of the tuff, along the crest of the ridge, an augite andesite crops out. This has a felsitic texture and under the microscope the plagioclase laths of the groundmass are seen to be in more or less parallel alignment, indicating a flowage structure. A few large phenocrysts of augite can still be recognized. Others have been altered into aggregates of epidote or brownish green biotite and secondary quartz. The matrix is composed of plagioclase laths, biotite, and augite.

This magnetite deposit is located about  $\frac{1}{3}$  mile northeast of the San Lorenzo batholith.

*Deposit at Outcrop No. 3*

The outcrop of the magnetite deposit at outcrop No. 3, which is  $\frac{1}{2}$  mile southeast of outcrop No. 2, though it is not very conspicuous at the surface, is of considerable interest because the relationship of the magnetite, and contact metamorphic minerals associated with it, to the Collores limestone is brought out more clearly than at the other outcrops. The magnetite associated with metamorphosed limestone occurs near the top of a northwest-southeast ridge. Numerous outcrops of nearly pure crystalline light gray and white limestone appear on the southwest flank of this ridge. The strike of the formations is N  $54^{\circ}$  W and the dip  $32^{\circ}$  NE. It is estimated that the limestone is at least 250 ft. thick. A small quarry has been opened from which limestone has been taken for burning into

lime for local use. Qualitative analyses indicate that the limestone should yield a good grade of lime.

A thin section of the crystalline gray limestone below the magnetite reveals an interlocking mosaic of calcite crystals of medium texture with only occasional minute grains of iron oxide among them and a very little chlorite. A specimen of the metamorphosed limestone from the hanging wall of the deposit is composed of garnet, pyroxene, and calcite, garnet being the most abundant. Garnet seems to have developed somewhat later than pyroxene and some of the calcite, in the form of little veinlets, cuts all three. Northwest of the deposit proper, prominent ledges crop out that range in mineral composition all the way from crystalline calcite associated with only small amounts of silicates to those in which silicates are the predominant constituents present. A thin section of the least-altered rock consists mostly of calcite and a little garnet intersected by fractures, along which quartz, specular hematite, and possibly magnetite, have been introduced replacing the calcite. This was followed by the development of chlorite along fractures and between calcite grains, replacing the latter in part. The final stage was the deposition of later calcite in the form of minute veinlets cutting the other minerals. Garnet showing pronounced optical anomalies is the predominating mineral in the more altered rock, having almost completely replaced the original calcite of the limestone. Magnetite and specular hematite have been introduced along fractures accompanied by the development of chlorite. Later veinlets of calcite and quartz cut the other minerals.

The limestone is overlain by an andesite at outcrop No. 3 and is underlain by a metamorphosed and much altered andesite tuff. The magnetite deposit occurs in the upper portion of the limestone, just below its contact with the overlying andesite. The San Lorenzo batholith lies about  $\frac{1}{8}$  mile to the southwest.

#### *Deposit at Outcrop No. 4*

Outcrop No. 4 occupies nearly the entire crest of a hill about  $1\frac{1}{2}$  miles southeast of outcrop No. 3. It has a length of nearly 200 ft. and a maximum width of 80 ft. at the western end, where some coarse micaceous hematite, associated with quartz, as well as massive magnetite are present. The outcrop, while not very large in area, is very prominent. Great boulders of massive magnetite derived from it are strewn along the hillside to the south and have accumulated in the little valley at the base.

A feldspathic andesite comprises the hanging wall of the deposit. Thin sections show it to possess a felsitic texture and distinct flowage structure brought out by the parallel alignment of the plagioclase laths. A few phenocrysts of plagioclase and a light green hornblende, derived possibly from augite, are present. Occasional aggregates of epidote also

occur. The matrix consists, predominatingly, of plagioclase laths in more or less parallel alignment. Skeleton crystals of iron oxide, possibly magnetite, are prominent; a little hornblende is also present. About 300 ft. south of the deposit there is a small outcrop of a sericite phyllite, probably representing a metamorphosed volcanic ash or shale, which has a strike of N 59° W and a dip of 41° NE; sericite, quartz, and iron oxides are its chief constituents. About 1500 ft. N 73° W from the deposit prominent outcrops of gray crystalline limestone and associated garnet rock were observed. The main San Lorenzo batholith lies  $\frac{3}{4}$  mile to the southwest, while a small offshoot from it crops out only  $\frac{1}{6}$  mile away.

*Deposit at Outcrop No. 5*

The magnetite deposit at outcrop No. 5,  $\frac{9}{10}$  mile south of Torres and about the same distance north of outcrop No. 4, does not belong to the

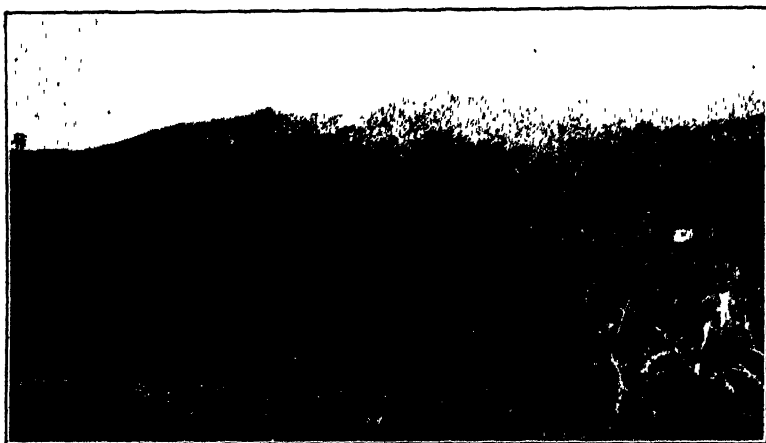


FIG. 6.—RIDGE WITH MAGNETITE DEPOSIT SOUTH OF TORRES.

same belt as the first four deposits. The outcrop, which is not very conspicuous and is traceable only for about 50 ft., occurs on the north side of a ridge just below its crest, which rises 410 ft. above the Gurabo valley; Fig. 6 shows the ridge as it appears from the north. Berkey<sup>6</sup> has described the deposit briefly.

On the northeast side of the ridge, 220 ft. below the magnetite prospect in elevation, outcrops of limestone are exposed, one ledge being 10 ft. thick. On account of the massive character of the rock, no strike and dip measurements on the limestone were possible. It is overlain, however, by an augite andesite showing flowage structure under the microscope, outcropping ledges of which occur in such relation to the limestone as to lead one to conclude that the strike of the contact of

<sup>6</sup> Charles P. Berkey: *Loc. cit.*, 55.

the two is N 48° W and the dip 52° SW. This makes it appear that a syncline occurs between the deposits of outcrops No. 4 and No. 5 and that the limestone at outcrop No. 5 may be the same bed with which the other four deposits are associated.

A microscopic examination of the limestone reveals a rather fine-grained rock composed chiefly of an interlocking mosaic of calcite crystals with occasional grains of quartz, augite, and plagioclase distributed among them. The latter undoubtedly represent tuffaceous material deposited contemporaneously with the calcareous constituents. About 170 ft. southeast of the limestone outcrops, along the hillside, a prominent ledge of vesuvianite rock, apparently developed from the limestone, was noticed.

Going in the direction of dip, augite andesite and latite occur between the limestone and magnetite outcrops over a belt about 350 ft. wide; whether these are extrusive or intrusive sheets could not be determined from their field relations. The andesite immediately overlying the limestone, in thin section, shows a parallel alignment of its plagioclase laths, indicating a flowage structure. The wall rocks of the magnetite deposit are not exposed. A latite tuff overlies the magnetite, but it was not observed in direct contact with it; this, in turn, is succeeded by dacites and andesites toward the southwest. The magnetite deposit lies  $1\frac{1}{8}$  miles northeast of the San Lorenzo batholith contact and  $1\frac{3}{8}$  miles southwest of the Luquillo stock.

#### ORIGIN OF MAGNETITE DEPOSITS

The magnetite deposits described are clearly of the ordinary contact metamorphic type. In each case, they occur in such relationship to the surrounding rocks as to lead to the conclusion that they have been formed by the replacement of a nearly pure limestone, a tuffaceous limestone, or a calcareous tuff, which are the kinds of rocks in which orebodies of contact metamorphic origin are most frequently encountered in other parts of the world. The iron minerals, namely, magnetite and specular hematite, are the minerals found in iron-ore deposits of contact metamorphic origin elsewhere, magnetite usually predominating as in the Porto Rican deposits. Small amounts of sulfides are usually encountered, in depth, in such deposits and the occurrence of small amounts of malachite in the outcrops described indicates that they are probably present in the deposits under discussion. The gangue minerals (amphibole, biotite, calcite, chlorite, epidote, garnet, pyroxene, quartz, talc, and vesuvianite) are such as are characteristic of ore deposits of the contact-metamorphic type.

A study of the geology of southeastern Porto Rico leads to the conclusion that the magma, which gave rise to the San Lorenzo quartz diorite batholith as well as the Luquillo and other smaller stocks and from

which the later intrusives that surround and in some instances penetrate the quartz diorite were derived by magmatic differentiation, was also responsible for the emanations that formed the magnetite deposits in the more calcareous portions of the "older series" of eastern Porto Rico. The proximity of the San Lorenzo batholith and the Luquillo stock as well as smaller offshoots to the magnetite deposits indicates that the quartz diorite undoubtedly underlies them at no great depth.

The metamorphism produced by the intrusion of the quartz diorite into the "older series" was of two kinds. In one case, it involved simply a recrystallization of constituents already present in the original rock with little change in chemical composition. The heat of the intrusive, and possibly the escaping water vapor, as well as the pressure exerted by mountain-making movements that accompanied the invading mass, were largely responsible for these changes. Hornblende schists were, in many instances, developed from andesite tuffs along the contact. In a few places, where the intrusive came in contact with shales and sandstone, phyllites and quartzites were formed. The conversion of an ordinary limestone into a crystalline one, such as now occurs in the vicinity of the magnetite deposits with the obliteration of all traces of organic remains, can likewise be attributed to the same cause.

In the case of the formation of the magnetite deposits and their associated silicates, on the other hand, emanations from the magma itself introduced large amounts of mineral matter, consisting chiefly of iron oxides and silica, which re-acted with and, to a great extent, replaced the original calcite of the limestone and calcareous tuff with which the deposits are associated. The occasional presence of vesuvianite indicates that fluorine may have been one of the mineralizers, in conjunction with water vapor, which aided in this transfer of material.

The mineralized emanations from the cooling quartz-diorite magma rose along fractures through the surrounding rocks, in the near vicinity of the intrusive, until they came in contact with the nearby limestones and calcareous tuffs, which re-acted with them much more readily than the andesites and ordinary tuffs with which they are interbedded. When making an exploration for iron-ore deposits in the area described, therefore, the belts along which the calcareous portions of the "older series" crop out are the ones that should be most thoroughly prospected.

## DISCUSSION

S. HERBERT HAMILTON, Philadelphia, Pa. (written discussion).—Some years ago, the writer made an economic study of the iron ore of eastern Porto Rico for clients in the iron business. That the iron ore is the result of contact between a basic eruptive and a limestone seemed obvious and was confirmed by microscopic studies by Harold Tomlinson, of Swarthmore, Pa. The writer is surprised that the author does not

lay more stress on the development of vesuvianite, so plentiful on Carranzana Mountain between Las Piedras and Boqueron (Torres). He does not mention a few copper minerals occasionally found at or near the contact; these were rare even in our excavations and would probably only be found by considerable pick and shovel work.

In regard to fossils, the writer must confirm the author's statements; even in the excavations, no fossils were found. However, near Peña Pobre, a limestone with minute fossils somewhat resembling *Palaeocyclas porvita* Lin. as figured by Zittel, page 74, but only about one-eighth inch diameter and somewhat more ovate, was found. On this scanty evidence the writer considered limestone to be older than the estimate given in the paper. The writer was also influenced by Gabb's report on Santo Domingo; of course the supposed coral may have been a large *Nummulite*.

The statement about the obscurity of the structure by surface conditions is only too true. The writer considered the position of the ore-bodies, together with the survey made by Mr. Jony and himself, to give an interpretation, without too great use of imagination, as follows:

With an apex west of Juncos and trending eastward toward Naguabo was a synclinal fold; this trough was considered to have had an eastward pitch. It was composed of limestone and along its margins and in its eastern interior it was attacked by basic eruptives. The result was iron ore, vesuvianite, and other contact minerals (no evidence of fluorine minerals was seen). The solution of the limestone and easily eroded minerals has given the large and misleading blocks of iron ore west of Juncos. East of Juncos, the two limbs of the syncline are made known by Esperanza (No. 1) and La Fe to the north (not mentioned by the author). Esperanza shows a north-south fault with a downthrow to the west. The valley between Esperanza Mountain and Carranzana Mountain, through which the trail from Las Piedras goes to Torres, is a cross-strike fault valley.

The iron ores of eastern Porto Rico, from an economic standpoint at least, are not magnetite and the title of the paper is misleading, although this is made plain by the reading matter. Economically considered, much of the ore is martite or hematite. The rather large samples taken by the writer and tested on Grondal type machines ran very high iron tails.

In the field, the erratic distribution of local terrestrial magnetism was also marked. For instance, the Esperanza and La Fe prospects on the north side of the river from Juncas gave a much poorer magnetometric map, by Tieberg-Thalen methods, than did prospects about 5 miles farther east. These prospects, between 4 and 5 of Fig. 1, made very poor surface showings but gave regular magnetic showings.

The commercial possibilities as given do not coincide with the writer's conception. Any commercial development must consider Ensanada

Honda as shipping point and the falls of Rio Blanca as a source of power. To attempt to take the ore to San Juan for shipment was carefully considered in conference with others in Porto Rico at the time, but was deemed impractical. Had transportation to the east coast existed and American bottoms been available, this iron ore would have been shipped years ago.

The author does not mention the commercial grade of the ore. Extensive sampling showed the ore to be about the bessemer limit in phosphorus, and otherwise to be a desirable iron ore with the exception of too high silica. The percentage of silica was in direct proportion to the earthy minerals present—mostly vesuvianite, garnet, epidote, hornblende and quartz. Experiments made on magnetic concentration were not satisfactory as so much of the iron was not magnetite. Magnetic cobbles would do little good on the intimately mixed minerals, and fine grinding with treatment on Grondal type machines gave high iron tails. No gravity treatment of tails from the Grondal or other magnetic machines were attempted, but a James capacity roughing table followed by a jig classifier might have made the milling problem look more practical.

Taking into consideration all the possible iron ore in eastern Porto Rico, perhaps 6,000,000 tons is an outside estimate of the tonnage in these orebodies. This would have to be cut to one-third, if only the possible commercial ore were considered and this 2,000,000 tons would include some ores rather widely scattered that would only be taken incidentally to a major mining industry. The known erratic nature of contact iron orebodies makes any close estimate of tonnage absurd. The other question, always uncertain in orebodies of this character that have not been highly developed, is the commercial grade of the ore. The talus blocks are quite misleading and the admixture of rocky minerals reduces the percentage much more as the effect of weathering is eliminated.

A. K. KNICKERBOCKER, Virginia, Minn. (written discussion).—In June, 1923, the writer spent ten days examining the magnetite occurrences described as Nos. 1 and 4 and made a hasty visit to No. 2, with a view to their exploitation. Deposit No. 2 did not appeal to him as a minable proposition. The magnetite is mixed with gangue minerals, garnet predominating, to a considerable extent. All assays extant showed this to occur to such an extent that the ore would be unmerchable from the standpoint of its silica content.

Deposit No. 4 is accurately described and at first sight is rather impressive. The outcrop is prominent and attains a considerable width. To the northeast, the float ore literally covers the surface in blocks of very high grade and pure magnetite of all sizes up to 6 ft. and 8 ft. in the long dimension. A day with the dip needle was disappointing. The body is of small lateral extent, being apparently, a stock or a short bulge in an otherwise narrow and unworkable vein. The deposit is also

rather inaccessible and undoubtedly has no economic value at the present time.

Deposit No. 1 was under option to a concern in 1906 or 1907, and the orebody, particularly the west quarter of it, has been explored to some extent. The orebody is more or less continuous for about 1800 ft., and has the characteristics of a vein, as it narrows and widens along its length and in places is nearly or entirely absent. A detailed investigation of the west 530 ft. of the orebody was made, the work consisting of cleaning out and reopening the 32 old pits, open cuts, shafts, and tunnels on that part of the property, and examining and sampling them. There are six tunnels driven into or through the vein; two of these tunnels we drove ahead a few feet to yield some necessary information. The lowest tunnel cuts the body about 75 ft. below the apex, most of the work having been done on top of the outcrop or short distances below it. A detailed dip needle survey of this area was also made. The deposit is in a long, narrow ridge rising about 300 ft. above the surrounding country. The magnetite outcrop forms the backbone of the ridge.

On the west 530 ft. of the body, the width varies from 12 ft. to 62 ft., the dip from 40° to 65° to the northeast, and the strike is constant at N 60° W. The average width of the orebody over the distance mentioned is 36 ft. The writer estimated 165,000 tons of ore proved on the length of 530 ft., taking 430 ft. of this distance to a depth of 75 ft., and the balance to a depth of 50 ft.

Analyses of carefully taken samples from the opening through the body showed:

No.	IRON, PER CENT.	SILICA, PER CENT.	PHOSPHORUS, PER CENT.	SULFUR, PER CENT.
1.....	66.80	4.45	0.065	0.034
2.....	64.40	5.40	0.058	0.007
3.....	66.60	4.50	0.055	0.027
4.....	66.40	4.30	0.058	0.028
5.....	63.10	6.45	0.062	0.030

The magnetite is everywhere high-grade where opened up in the area investigated in detail. As shown, sulfur analyses are low and no evidences of the removal of pyrites could be noticed in the orebody proper, though toward the east end of the 530 ft., in what appeared to be a separate lens of garnetiferous magnetite of low iron tenor, lying south of the main body, several stains of copper were seen over a distance approximating 100 feet.

The author mentions Fajardo Playa and San Juan as two possible ports of export. There is a well-constructed 1-meter railroad running from Humacao Playa on good grades through Humacao and Rio Piedras and west to a point near Juncos, where it connects with the railroad owned by the Central Juncos; this railroad is owned by Senor Antonio Roig, of Humacao. It runs along the southern foot of the ridge con-



taining orebody No. 1 and as the owner is desirous of increasing the tonnage of his road would make an attractive rate. The down-grade haul from the west end of the property to the port of Humacao is 11 miles. The transportation problem is thus a relatively easy one. The port will accommodate vessels of 26 ft. draft.

The dip-needle work tended to indicate, what has been deduced by the authors from geological inferences, that the orebody does not extend, in all likelihood, for a great depth. The deposit is one of interest and presents the possibility of the development of 1,000,000 to 3,000,000 tons of ore, of good merchantable grade. The property undoubtedly offers encouragement for drilling at some future time, both to determine the width and extent of the body at depth and the sulfur content below the leached zone.

CHAS. R. FETKE (author's reply to discussion).—The author did not feel warranted in making any estimates of tonnages available based on observations on the outcrops alone and is particularly interested to see the estimates arrived at by Messrs. Hamilton and Knickerbocker, who had an opportunity to do some exploratory work. The two estimates, arrived at independently, are practically in accordance and are about what the author would have made if he had hazarded a guess.

The ores examined by the author did not contain vesuvianite as an abundant gangue mineral, as did those examined by Mr. Hamilton. Some of the massive andradite garnet, which in thin section shows birefringence and is optically negative, was at first mistaken for vesuvianite, but index of refraction determinations revealed its true character. The author realizes that specular hematite is an important constituent of the ore but believes that it is second in importance to the magnetite, which predominates in most instances.

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## South Lorrain Silver District, Ontario

By J. MACKINTOSH BELL, M.A., PH.D., TORONTO, ONT.

(Canadian Meeting, August, 1923)

IN THE numerous districts subsidiary to Cobalt, and carrying mineral deposits similar in character to that world-famous mining camp, the most interesting recent developments have occurred in South Lorrain. The district, the center of which lies about 16 miles southeast of Cobalt, was the scene of a rush in 1907 but, in spite of the success of the Wettlaufer mine, the locality soon lost its popularity, largely on account of the unsavory early history of the Keeley mine. In recent years, following the successful development of this property by the London operators, who acquired it from the liquidator of the original company, and the later conspicuous progress made on the properties of the Mining Corporation contiguous to the Keeley on the north, the district has again come into prominence and, at present, is doing much toward maintaining the gradually declining production of Cobalt itself.

Apart from the Mining Corporation of Canada and the Keeley Silver Mines Limited, the principal concerns now operating in South Lorrain are the Lorrain Consolidated, the Trout Lake Mines (operated by English interests associated with the Mining Corporation) and the Canadian Lorrain Silver Mines (operated by the Huronian Belt Co., of London). A number of minor prospects are also active. The Wettlaufer and Currie, on both of which considerable work was done some years ago, are now closed.

### TOPOGRAPHY AND GENERAL GEOLOGY

The topography of the South Lorrain area is rather more rugged than that of the vicinity of Cobalt, but the local relief, relatively speaking, is not great. Numerous lakes and streams lend a certain picturesqueness to a landscape, which is not entirely marred by the absence, from the valleys and hillsides, of the splendid bush that formerly clothed them but which has been swept away by forest fires.

The geology of the locality is simple, in a lithological sense, but rather complicated structurally. The oldest rocks are Keewatin greenstones

above which follow, in the order named, lamprophyre dikes, Lorrain granite, the Cobalt series (conglomerates, slates, and quartzites), and Nipissing diabase. A few acidic dikes are found, which are probably later than the diabase. Rocks of the Temiskaming series, consisting of conglomerates and other fragmentals, which unconformably overlie the Keewatin near Cobalt, are absent in South Lorrain, nor are there any exposures of Silurian strata, such as are common on the islands of Lake Temiskaming and elsewhere farther north.

#### GEOLOGICAL SEQUENCE OF THE COBALT DISTRICT

Pleistocene: Glacial clays, sands, etc.

Paleozoic: Niagara limestone.

Pre-Cambrian:

Later dikes (both basic and acidic).

Nipissing diabase (intrusive contact).

Cobalt series (conglomerates, slates, quartzites).

#### Unconformity

Lorrain granite (intrusive contact).

Lamprophyre dikes (intrusive contact).

Temiskaming series (conglomerates and graywackes).

Keewatin: Complex of schists of various types, ironstones, etc.

At Cobalt, the silver-bearing veins occur in Keewatin rocks, in those of the Cobalt series, and in diabase, though more than 90 per cent. of the production has come from one formation—the Cobalt conglomerate (Cobalt series).<sup>1</sup> In South Lorrain, the production, up to the present, has been entirely either from the Keewatin greenstone (and associated lamprophyre dikes) or from the Nipissing diabase.

The Nipissing diabase, in South Lorrain, occurs in the form of a wide sill that, after being folded into a broad dome, was subjected to pronounced faulting and long-continued erosion. Today, the center of the formerly continuous dome is mainly a valley underlain by rocks of the Cobalt series and occupied by numerous small lakes, the largest of which are Loon and Oxbow. Along the outer slopes of the dome, Keewatin rocks are conspicuous; these, in turn, are generally overlain by rocks of the Cobalt series. Silver ores in appreciable quantity have been found in two localities only, namely along the western slope, where are situated the Keeley and the properties of the Mining Corporation, and along the northeastern slope, where the Canadian Lorrain silver mine is situated. The latter area is unimportant and, for the purpose of this paper, only the area adjacent to the Keeley and the properties of the Mining Corporation need be considered.

It is not proposed to give a detailed petrological description of the rocks directly associated with the silver veins. They do not differ materially

<sup>1</sup> W. L. Whitehead: The Veins of Cobalt, Ontario. *Econ. Geol.* (1920) 15, 128.

from similar rocks at Cobalt, which have been frequently described.<sup>2</sup> The greenstone is ordinarily of fine texture and so metamorphosed that its original character is difficult to identify. A petrographical range from andesite to basalt is suggested. A coarser greenstone, probably an altered diabase, is conspicuous in places and elsewhere amphibolites are found.

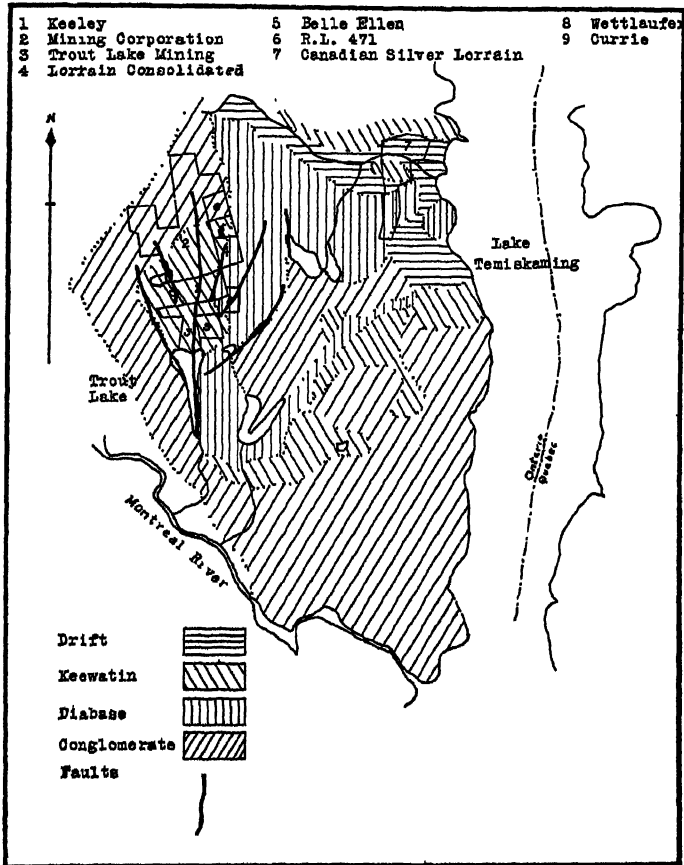


FIG. 1.—SKETCH MAP OF SOUTH LORRAIN, SHOWING GEOLOGY AND PRINCIPAL CLAIMS.

The lamprophyre dikes, which ramify in all directions through the Keewatin greenstones, are, in places in proximity to the veins, difficult to distinguish from the later Nipissing diabase; but, ordinarily, the considerable shearing of the lamprophyre, together with large flakes of an altered mica and of chlorite therein, serve to differentiate the two.

The strike of the contact between the diabase sill and the intruded Keewatin greenstone near the Keeley is approximately north and south,

<sup>2</sup> W. G. Miller: Report of Bureau of Mines, Ontario, 19, II, 45; A. G. Burrows: South Lorrain Silver Area. Report of Bureau of Mines, Ontario, 19, II, 134.

and the dip westerly at angles varying from  $10^{\circ}$  to  $30^{\circ}$ . The depth, below the surface, of the diabase beneath the Keewatin, westerly of the contact, however, does not conform to these angles; it is complicated by a variety of major north and south reverse faults and by others of lesser importance, transverse to the major features, and by minor rolls.

### CHARACTER OF THE VEINS

The silver-bearing veins of South Lorrain resemble so closely those of Cobalt (which have been frequently described<sup>3</sup>) in most particulars that it will be advisable to emphasize the differences rather than reiterate characteristics that are well known and common to both localities.

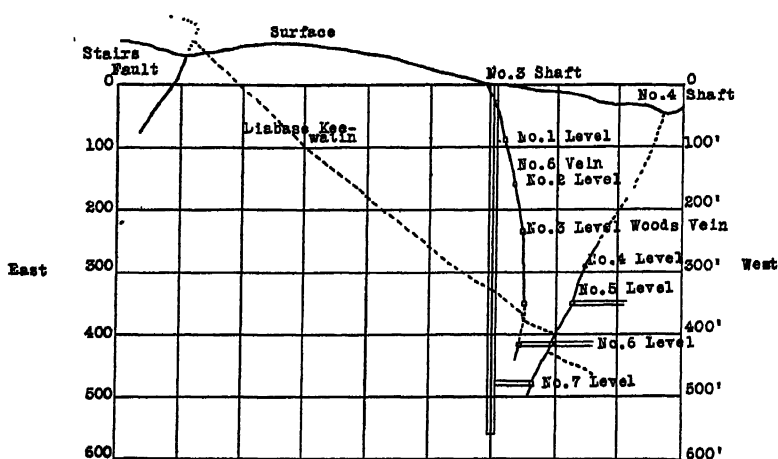


FIG. 2.—TRANSVERSE SECTION THROUGH SHAFTS NO. 3 AND NO. 4, KEELEY MINE, SHOWING MAIN VEINS AND FAULTS.

As at Cobalt, the principal metallic minerals occurring in the veins are cobaltite, chloanthite, smaltite, niccolite, pyrite, marcasite, mispickel, chalcopryite, native silver, argentite, ruby silver in various forms, and native bismuth. Galena and sphalerite, which are comparatively rare in Cobalt, are relatively common in some of the veins in South Lorrain; covellite, stromeyerite and dyscrasite are comparatively uncommon.

Much of the vein material is composed of altered country rock, which is more or less replaced by carbonates (chiefly calcite with some dolomite) and quartz, or by the metallic minerals previously indicated. Other non-metallic minerals found in the veins are apatite, tremolite, and biotite.

<sup>3</sup> W. G. Miller: *Loc. cit.*, 5.

Cyril W. Knight: Cobalt, Its Past and Future. *Eng. & Min. Jnl.* (1922) 113, 761.

Edson J. Bastin: *Econ. Geol.* (1917) 12, 219.

Alfred R. Whitman: University of California Publications. *Geol. Sci.*, 13, 253.

W. L. Whitehead: *Loc. cit.*

While impregnation of the adjoining country is found 5 or 6 ft. from the vein proper, this favorable feature is less conspicuous in South Lorrain than at Cobalt, and the veins are essentially narrow, generally varying from a few inches to a few feet in width. However, some of the principal veins do not always occupy a single fracture, but commonly a fractured zone, which may be 10 ft. in width, contains a number of parallel deposits.

The length of some of the veins of South Lorrain is remarkable. Wood's vein, which may be described as the mother lode of the western, or what is now the only productive, part of the locality, has been traced from the Trout Lake ground right across the Keeley and apparently as far north as the Forneri claim of the Mining Corporation; or a distance of over a mile in a north-and-south direction. The pronounced fault that it occupies resembles the Cobalt Lake fault, in being the controlling factor in influencing the distribution of the veins, but it differs therefrom in the remarkable strength and richness of the vein material and in the much smaller quantity of gouge.

Parallel to Wood's vein occur a number of other "north and south" veins, and subsidiary to it are such important producers as the No. 16, No. 20, and No. 26, on the Keeley, and the "Watson," on the property of the Mining Corporation, which fork from the parent deposit in various directions. The Wettlauffer vein, on the property of the same name, which for a time was such a heavy producer, is apparently connected with a fault zone lying to the east of those conspicuous on the Keeley and Mining Corporation properties.

The fact that the principal veins in South Lorrain occupy pronounced faults, rather than mere fractures as at Cobalt, forms an important point of difference between the two localities. Another interesting feature, which is in contrast with conditions at Cobalt, is the relatively deep-seated oxidation in South Lorrain, especially in the Keeley. While most of the Keeley veins show only superficial oxidation, No. 1, No. 2 and No. 4 veins in the northern part of the property are slightly oxidized to a depth of over 100 ft., and the southern part of Wood's vein and the strong deposit, No. 20, branching therefrom, show marked oxidation to the deepest level at present developed, namely 480 ft. Not only are Wood's vein and No. 20 oxidized, but the alteration extends into the foot walls of each, and into various small stringers branching from their hanging walls. The oxidation at the deepest horizon yet reached does not consist merely in the change of iron sulfides to oxides, or of the removal in places of all the carbonates and of the cobalt- and nickel-bearing minerals, but in the complete alteration to a clay-like material, in which the only metallic minerals are native silver (generally in wire form) and argentite. It is noteworthy that where the oxidation is complete, that is where ferric rather than ferrous conditions are conspicuous, even the

silver minerals are absent. In the upper levels of this southern part of the Keeley mine, the alteration is naturally more intense than at deeper horizons, and for relatively long distances the vein material consists of what can best be described as a red and yellow clay, with metallic minerals present only where lenses of ferrous material occur.

It would seem unreasonable to suppose that such deep-seated oxidation can all be post-glacial,<sup>4</sup> especially as the surface depression, which occupies the outcrop of Wood's vein, is relatively deeply filled with boulder clay. Rather it would appear more natural to consider that the oxidation antedated the glacial period and that the greater depth to which it extends in the southern than in the northern part of the Keeley is probably to be connected with the position of the water level in a pre-glacial topography, the nature of which is not now clear. It seems possible that glacial denudation was not as great in Cobalt as in portions of South Lorrain and that in the southern, and particularly narrow, part of the depression occupied by Wood's vein, protection against corrosion was given by the walls of greenstone on either side, especially after the depression had been filled with débris with the initial advance of the ice.

### THE ORESHOOTS

In both of the producing properties in South Lorrain, numerous oreshoots have been discovered varying in length from a few feet to more than 100 ft. On the Keeley, there are several shoots of mixed milling and high-grade ore over 200 ft. in length, averaging over 200 oz. across 3 or 4 ft., and one oreshoot (F-D) attains at one horizon a length of 400 ft.

While these oreshoots are ordinarily shorter than they are at Cobalt, what they lose in length they make up in width and richness. For example, at one point in the Birthday bonanza of No. 26 vein of the Keeley, massive ore, consisting of cobaltite or smaltite and native silver, reached a width of 5 ft. of material running more than 7000 oz. to the ton. This remarkable bonanza has not yet been stoped, and it is thus impossible to say how much silver it will contain; but an idea of the extent and richness can be gathered from the fact that from the drift at which it was developed on the 480-ft. level, no less than 350,000 oz. were taken from its length of approximately 75 ft. A wonderful shoot of ore has been partly mined on Wood's vein on the Crompton claim of the Mining Corporation, and already, from a length of less than 100 ft. and an extension along the dip of less than 100 ft. over 1,000,000 oz. have been drawn.

The oreshoots in South Lorrain seem, too, to have a greater vertical range than those of Cobalt. The D shoot of Wood's vein on the Keeley has been traced and partly mined from the surface downward to a vertical

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<sup>4</sup> Henry H. Knox: *Econ. Geol.* (1922) 17, 655; J. B. Tyrrell: *Econ. Geol.* (1928) 18, 296.

depth of over 450 ft. or an extension along the dip (which averages about  $60^{\circ}$  easterly) of about 550 ft. The oreshoot above 400 ft. (vertical) is entirely in greenstone; and from that point to 450 ft., the foot wall is greenstone and the hanging wall diabase.

Certain generalities that govern the position of the oreshoots in South Lorrain, as also, within limitations, those at Cobalt, may be enumerated:



FIG. 3.—FACE OF BIRTHDAY BONANZA.

1. Generally speaking the richest and most persistent oreshoots occur at or near the diabase-Keewatin contact, either within the diabase or within the Keewatin; the immediate contact is commonly barren or of low grade.

2. The junction of one vein with another, even a considerable distance from the contact, affects the values, either in one vein or the other, or in both. If the veins are valueless before joining, an oreshoot of greater or less length is commonly made in the united vein.



3. The values within a sufficient distance of the contact, even in the smaller veins, are likely to improve when the deposit occurs in a well-fractured zone, with cracking developed parallel to its strike.

4. Oreshoots are frequently localized on a main vein between the points of departure of two minor branching veins, or between the points of crossing of two zones of fracturing.

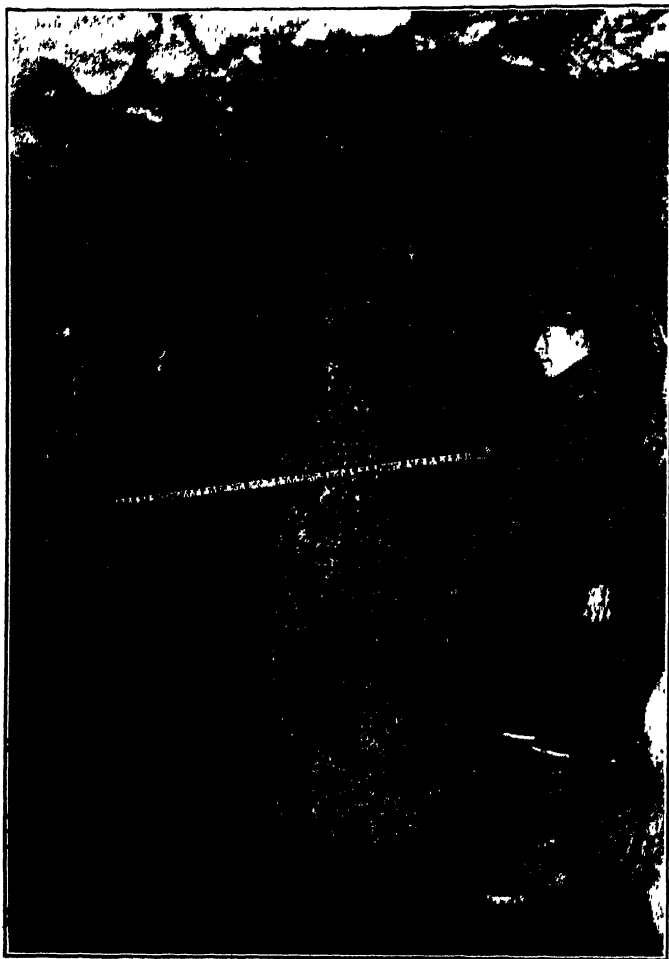


FIG. 4.—FACE OF JOWSEY BONANZA.

5. When the oreshoots are in Keewatin rocks, the most favorable rock is an extremely dense, fissile, well-fractured greenstone. Lamprophyre is generally less favorable, though some of the richest ore is found in fault planes where greenstone occupies one wall and lamprophyre the other.

6. Generally speaking, the veins are more likely to carry ore where the dip of the vein is steep (upwards of  $70^{\circ}$ ) than where it is flat. Wood's

vein, however, carries large amounts of ore when the dip is as low as 60° or even less.

7. It is noteworthy that where the dip of a vein varies from the vertical in both directions, one inclination may be productive and the other not.

The origin of the veins of South Lorrain, with their rich oreshoots, is similar to that of Cobalt, where the question has received much attention from various authorities.<sup>5</sup> The writer has given his opinions in this connection elsewhere<sup>6</sup> and considers it unnecessary here to do more than repeat his conviction that while the greater part of the ore is primary and due to hypogene agencies, there has been, in places, material enrichment by descending solutions that derived their silver content from the now impoverished portions of the oxidized zones.

### MINING AND METALLURGICAL PRACTICE

The mining methods and metallurgical practice in South Lorrain present little or no variation from those in vogue at Cobalt and, consequently, need not be discussed here. Both the Keeley and its neighbor to the north have small but adequate mining plants. The mining corporation has, as yet, no mill; the lower grade milling ore is stacked or left in the mine, while the high-grade and richer milling ore is sent to the company's plant at Cobalt for treatment.

The Keeley has a simple, but effective, milling plant, which is being increased from 70 to 140 tons. After coarse primary crushing, the oversize is passed over a picking belt, for removal of the high-grade ore. A secondary crushing follows, and then further comminution either by stamps or ball-mill, or both, depending on the nature of the material treated. Subsequent treatment is by concentration on various tables of Wilfley or James type, with final cleaning in an oil-flotation unit.

Considerable difficulty has been experienced in treating the oxidized ore; but it is hoped the troubles in this connection will, to a large extent, be overcome by minor changes now being made in the plant. Generally speaking, the percentage of extraction increases in direct proportion with the grade of ore treated; it averages about 90 per cent.

### PRODUCTION

Up to July, 1923, South Lorrain had produced approximately 6,500,000 oz. of silver, distributed, roughly as follows:

	OUNCES
Wettlauffer.....	3,000,000
Keeley.....	2,000,000
Mining Corporation.....	1,500,000

<sup>5</sup> See previous references and also A. R. Whitman: *Diffusion in Vein Genesis at Cobalt*. *Econ. Geol.* (1920) 15, 138.

<sup>6</sup> J. Mackintosh Bell: *Bull. Inst. of Min. and Metal.* (February, 1922).

## DISCUSSION

E. T. MCCARTHY, London, England (written discussion).—On page 1049, the author says "Certain generalities govern the position of the oreshoots in South Lorrain, as also, within limitations, those at Cobalt may be enumerated." He sums these up in seven paragraphs, and with all of these statements I agree; but regarding the theory of the origin of their deposition he refers to various authors and to his own opinion given elsewhere. My opinion, so far as the upper oxidized parts of the mine referred to in the paper are concerned, is in conformity with the author's; but when we come to the primary ore, we know little in regard to its position in the mine. Much has been written on ore magmas, notably J. E. Spurr's two recent volumes, but no one seems to offer a reasonable solution of the question of ore "position" in veins. Why, for example, should we get the richest silver ore near the contact of the diabase with the Keewatin; or on a main vein between two points of departure of two minor branching veins; or, yet again, affected by the dip of the vein? Numerous explanations are offered but until we know something more about the conditions under which ore magmas exist under great pressure and at different temperatures, and also how they may be affected by electric currents, it looks as though we had reached a point where we are at a standstill, or nearly so. Meantime, such observations and recording of facts as are given in this paper are invaluable in adding to our knowledge of ore deposits. Although we may not know the whole of the conditions governing the deposition of ore, in the case of this silver field the author has demonstrated that mining geology has now advanced to a degree where fairly safe deductions can be made and acted upon.

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## Recent Exploration for Petroleum in the United Kingdom

By E. L. ICKES, ZELZAH, CALIF.

(Tulsa Meeting, October, 1923)

DURING the summer and winter of 1918 eleven standard rigs were erected in the United Kingdom to test the petroleum prospects of ten structures, eight of which were in England and two in Scotland. By the fall of 1921 ten of the wells were completed; the remaining one, the D'Arcy in Scotland, was stopped some months later. The tests were deep ones, five of the wells being 4000 ft. or more, the rest varying in depth between 1810 and 3918 ft. The total footage drilled was 40,047 ft. The holes were put down with standard or cable tools purchased in the United States (except the boilers). The larger sizes of casing, 10-in. and above, were also from America, while the smaller sizes were secured in Scotland.

The Hardstoft well in England found a small production of high-grade oil and the D'Arcy well also encountered what is reported as a favorable showing at a depth of 1810 ft. The Werrington and West Calder wells had to be abandoned on account of drilling difficulties. The Apedale well encountered great thicknesses of ash in the Carboniferous and had to be abandoned on account of depth. The results might be summarized by saying that of the ten structures drilled upon, two yielded encouraging showings; three cannot be considered as having been adequately tested; and five produced dry holes, although in some of these small oil showings and gas were met.

The total cost of the work amounted to about half a million pounds sterling, which sum includes the cost of all equipment, subsequently sold by the government. The work, under the superintendence of V. L. Conaghan, took place for the most part in the period immediately following the war—a period of high prices, labor and transportation difficulties, and unsettled conditions generally; factors tending to retard the work and affect the costs.

The writer, as a member of the staff of S. Pearson & Son, Ltd., had charge of the administration of the work during its later stages and

therefore had recourse to the various details of operation. In this account he regrets being unable to enter as fully into a geological discussion as might be desirable, due to inability to consult the required references and notes.

During continuance of the drilling, progress reports were issued by H. M. Petroleum Department, and some accounts have appeared in publications of H. M. Geological Survey. The chief paper so far dealing with the subject is by Veatch,<sup>1</sup> and the present paper will in a measure supplement that.

The drilling campaign was undertaken as a war measure, for in 1917 the oil shortage for war purposes became so acute, because of the activity of the German submarines, that it was imperative to ascertain as soon as possible the value of home oil prospects. The firm of S. Pearson & Son had been looking into the oil question for some time and was at this period intending to drill several test wells. In the summer of 1917, the Government, on account of the firm's knowledge of the oil business and the information it had collected on British oil, approached Lord Cowdray, the head of the firm, with a view to immediate drilling as a war measure, and proposed taking up the work itself if Lord Cowdray was not prepared to do so. At this time the British Government was spending nearly eight million pounds sterling daily in the prosecution of the war, in comparison to which the cost of a few test wells would be small while the results, if successful, would be of the greatest value to the nation. Accordingly, Pearsons were made agents and given the supervision and direction of the work (the services being without compensation), and men and machinery were ordered in America. For drilling purposes, it was necessary to take the sites under Defense of the Realm Acts, which were war regulations of a temporary nature. The wells were scattered, to try out various conditions. Most of the wells were not going until shortly after the Armistice, and the ending of the war altered the plan of drilling campaign. The results achieved justified the undertaking and expenditure incurred. Oil was proved; and although it was not possible to extend and develop the findings brought forth by the drilling, on account of the limitations under which the work was done, the tests were of a comprehensive nature and will afford a valuable guide in future prospecting. In a country like Great Britain, with its large population, excellent transportation, ready oil market, mild climate, and other facilities, a small well is more apt to be a commercial proposition than a similar well in other countries. What might be considered as unfavorable aspects from the wildcatter's standpoint are the difficulties in the way of securing land readily and the obstacles liable to be encountered from the

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<sup>1</sup> A. C. Veatch: Petroleum Resources of Great Britain. *Trans.* (1921) 65, 7.

mining interests, who would not view any too kindly the location of a well near a mine workings.

### GENERAL GEOLOGICAL FEATURES

The English wells were located in the Midlands, an important industrial region occupying the heart of England about 125 miles northwest of London. In point of superficial distribution and structure, England may be divided into two parts: the flat-dipping Mesozoic and Tertiary rocks covering the eastern, southeastern, and southern portions of the country and the outcrops of Carboniferous and older rocks, which form the western and northern portions. The older areas show more deformation and usually give rise to a more rugged topography. Belts of Mesozoic also occur in the older rocks and a notable depression filled with the younger formations crosses the country, in a northwesterly direction, through the south Midlands, Cheshire and Liverpool, and separates the older rocks of Wales from those of central England.

As would be expected, the two groups are separated by a marked unconformity. Borings starting in the Mesozoic, on reaching the Paleozoic floor beneath, sometimes encounter Carboniferous, as in the case that led to the discovery of the concealed Kent coal field southeast of London; or the drill may strike Devonian, Silurian, or other formations, which make up the floor upon which the younger rocks are resting.

The outcropping rocks of the north of England are moderately deformed Carboniferous. Along the Scottish border, these are interrupted by a wide belt of highly folded Silurian with a northeasterly trend; beyond this belt in central Scotland, the Carboniferous reappears in an isolated basin in the vicinity of Glasgow and Edinburgh. On account of this interruption in their continuity, there is some difficulty in correlating the Carboniferous members of the two countries.

All the borings started, and presumably ended, in the Carboniferous. Those in England were in two groups: one on the east side of the Pennines in Derbyshire, the other on the west side in North Staffordshire. The Scottish wells were located in the Carboniferous basin near Edinburgh.

The Pennine Chain is sometimes referred to as the "backbone" of England. It starts north of Derby, coincident with the appearance of the Carboniferous, and continues north through the mid-portion of the country to the borders of Scotland as a series of hills and tablelands rarely attaining an elevation over 2000 feet.

### INDICATIONS OF PETROLEUM

Oil manifestations of various types can be said to be of general occurrence in certain districts of the United Kingdom. They range in

character from veinlets and fragments of bitumen and wax through outcropping oil sands to actual seepages. At some place or other, practically every formation from the pre-Cambrian to the Cretaceous can be found to contain one or more of these types. A characteristic of most of the fluid varieties from the Paleozoic is the high wax content, causing the oil to set at ordinary temperatures. Many occurrences have been discovered in coal and lead mining operations, from early times; most of the indications have been found associated with the Carboniferous and most of these are located in the Midlands and Scotland. We will begin the description of some of the occurrences with Derbyshire.

At Riddings colliery, situated on the crest of the fold tested by Ironville well No. 1, oil was found in the Kilburn coal workings of the lower coal measures. For several years, about 1850, James Young utilized this oil and separated such fractions as kerosene, lubricating oil, and wax. On the exhaustion of the supply, either through abandonment of the workings or cessation of the seepage, Young, believing the oil was derived from coal, experimented with Scotch torbanite, which gave somewhat analogous products on distillation, and transferred his operations to Scotland and founded the oil-shale industry. It appears from an account by Marshall<sup>2</sup> that oil was found in the same mine and used locally about 20 years later but whether it was the same locality as that used by Young is not clear. The yield at this time was about two barrels per day for two years and near an important fault crossing the fold. Stokes<sup>3</sup> speaking of the same mine says that in some years 100 tons were obtained and sold for £7:10:0 per ton, or about \$5 per barrel. Another well-known seepage was located in the workings of Clowne colliery a few miles east of the Renishaw well. Here in a smashed zone between two faults in the Top Hard coal horizon of the productive coal measures seepages were found over an acre or so in area, the yield being reported as high as 14 bbl. per day at one time. Just north of the Derbyshire line, at Manvers Main colliery, a few miles northeast of Sheffield and situated on a broad anticlinal nose, large seepages were encountered some decades ago. According to Cohen and Finn,<sup>4</sup> the oil came from the roof of the Parkgate seam of the productive coal measures and for days the yield was 100 bbl. per day of oil. Oil is reported from other collieries on this side of the Pennines, usually with faults. In the concealed coal field to the east, where the coal measures of Derbyshire dip under cover of the Mesozoic, a 13-ft. oil sand was found in the Kelham boring in the Mill-

<sup>2</sup> R. A. Marshall: Mineral Oil as Found at the Deep Main Pits, Riddings, Derbyshire. *Trans. N. Staff. Inst. Min. Eng.* (1879) 1, 126.

<sup>3</sup> A. H. Stokes: Economic Geology of Derbyshire. *Trans. Chesterfield Inst. Eng.* (1878) 6.

<sup>4</sup> J. B. Cohen and C. P. Finn: Paraffines from a Yorkshire Coal Seam. *Jnl. Soc. Chem. Ind.* (1912) 31, 12.

stone Grits, and a 10-ft. sand at the Retford boring in the coal measures, while prospecting for coal with the diamond drill. These oils were of the same character and were under sufficient pressure to force small amounts to the surface against both 3000-ft. water columns.

The upper part of the Mountain Limestone adjoining the west side of the Derbyshire coal field was at one time actively mined for lead and spar; in some of the workings pockets of oil were found, and in the overlying Limestone Shales enough gas to cause fatal explosions. Short<sup>5</sup> two centuries ago writing of the Hucklow Edge lead vein says that the vein for several miles was overlaid by a bed of boulder stones each yielding from  $\frac{1}{2}$  pint to 1 gal. of soft bitumen like Barbadoes tar, and that there were springs of oil in the mines which on catching fire would burn for days at a time. Pilkington<sup>6</sup> and Farey,<sup>7</sup> writing a century later of the mines in the same region, mention how the miners would burn the oil in their lamps and how the oil, covering the water in the mines and catching fire, would burn for some time and give rise to "burning springs."

Nor is surface evidence wanting that oil may have occurred in the upper limestone. The writer has seen more abundant evidence in the limestone of Derbyshire than in the Tamasopa limestone outcrops of Mexico. On the crest of the Crich dome, 6 miles west of the Ironville wells, Fig. 1, oil can be found filling vugs in the limestone. In the top of the limestone at Castleton, west of the Ridgeway well, is a large patch or seepage of elaterite and, in the same vicinity, gash veinlets filled with hard and soft bitumen and wax and cavities with oil can be found, especially around the ancient Odin lead mine, which has been worked from time to time since the days of the Saxons. Oil in this mine has been mentioned by various writers. Without reference to the other occurrences on the east flank of the Pennines, we will mention a different type at Burton, 12 miles south of the town of Derby. A road cutting here exposes about 30 ft. of flat Triassic sandstone, a good deal of which has a chocolate color due to oil and yields, by solvents,  $2\frac{1}{2}$  per cent. of petroleum, having the characteristics of Carboniferous oil. This horizon is traceable on the surface for  $1\frac{1}{2}$  miles, and may at one time have been a well charged pool, derived through faults from the Carboniferous lying a few hundred feet below.

On the west side of the Pennines, in Staffordshire, at the Meir Hay colliery, well down on the flanks of the fold upon which the Werrington well was located, sufficient seepage oil was obtained to justify the erection

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<sup>5</sup> Dr. T. Short: "The Natural Experimental and Medicinal History of the Mineral Waters of Derbyshire, Lincolnshire and Yorkshire." London, 1734.

<sup>6</sup> J. Pilkington: "A View of the Present State of Derbyshire." London, 1789.

<sup>7</sup> J. A. Farey: "General View of the Agriculture and Minerals of Derbyshire." London, 1811.



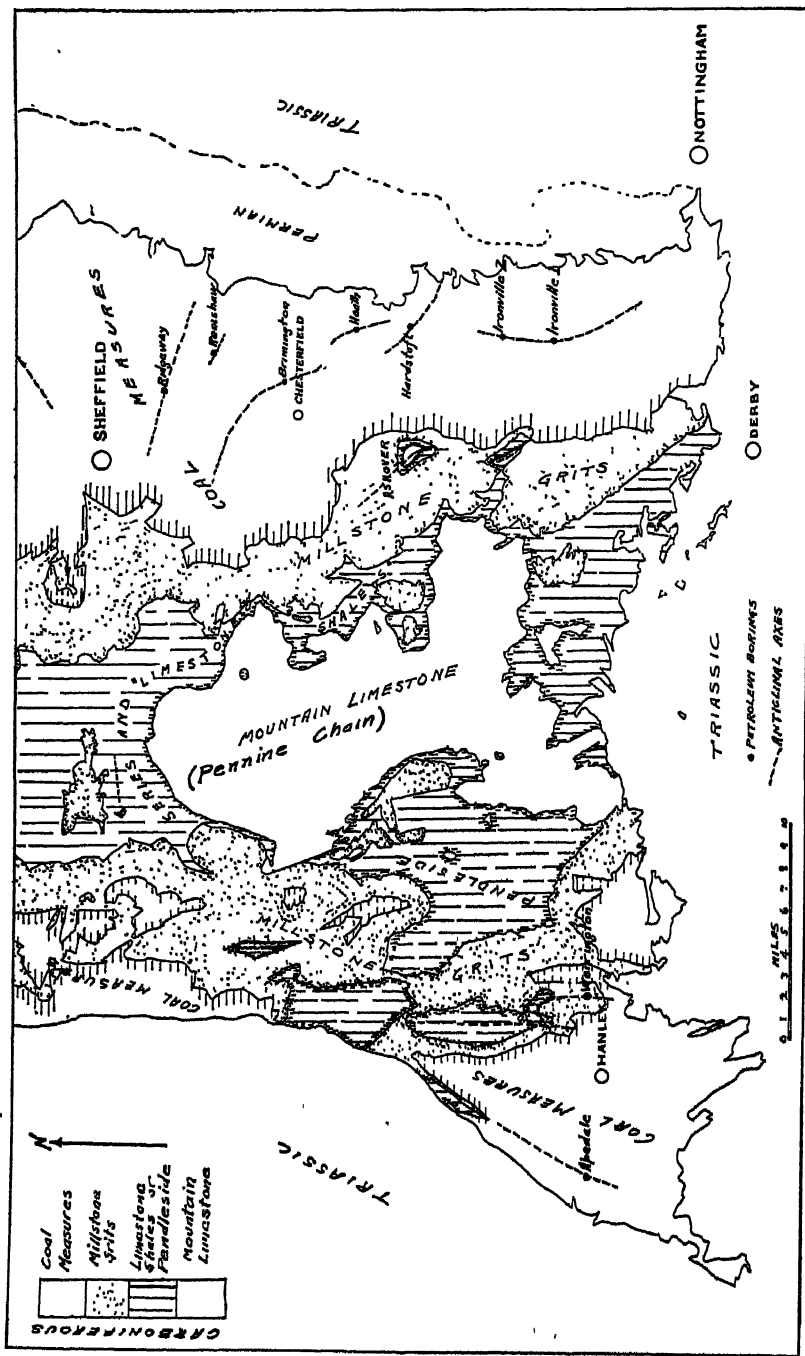


FIG. 1.—GEOLOGICAL MAP OF PORTION OF MIDLANDS OF ENGLAND; GEOLOGICAL BOUNDARIES ARE TAKEN FROM GEOLOGICAL SURVEY MAPS; FOLDS ARE FOR MOST PART BASED ON MINING AND OTHER SOURCES.

of a small refinery in 1874. The owner, a Mr. Walker<sup>8</sup>, secured some 5 bbl. per day for a year or two when the pits were closed down, after which he secured a like amount for a year or two from an adjoining colliery. The oil contained 15 per cent. of wax and yielded a good grade of kerosene. On the west side of this coal field, small oil seeps are found in the coal workings on the east and south flanks of the fold drilled by the Apedale well. Samples collected during the work were charged with wax and were chemically similar to the limestone oils. A seepage from the Fair Lady pit, described by Peasegood,<sup>9</sup> and adjoining an overthrust fault, had a gravity of 37° Bé. and carried 4 per cent. gasolene, 9 per cent. kerosene, and 5 per cent. wax.

In the worked-out Coalbrookdale coal field, 30 miles southwest of the North Staffordshire area and close to the border of Wales, the coal measures and lower Carboniferous are thin, moderately flexed but considerably faulted. This district is noteworthy in the large amount of seepage material in evidence, as well as the written accounts dealing with the oil found in the past. Half a mile east of the village of Coalbrookdale, at a quarry called Oil House Coppice, is exposed a tar sand over 15 ft. thick oozing black oil and traceable a mile on the surface, the horizon being at the base of the coal measures. Under Coalport postoffice, in the same field, is an old mine level the walls of which are coated with thick oil and tar for a few hundred feet. A century ago, this seepage supplied oil for a remedy known as "Bettons British Oil," and in 1865 Mr. Holmes, an American, tried to lease the land for drilling purposes from Lord Forrester. Referring to a seepage a few miles to the east, where the sandstone still shows a little oil, Prestwich,<sup>10</sup> writing some hundred years ago, says "In a pit at the top of the same dingle petroleum exudes in so great abundance . . . that the colliers were obliged to have large plates of iron suspended over them." From the Pitchford seepage, in the same general district, the Romans are reported to have secured pitch for the construction of their camp at Wroxeter, nearby. Elele,<sup>11</sup> writing over two hundred years ago, apparently refers to this place in describing a crude refining process on a "blackish stone which is porous and contains in it great quantities of bituminous matter." On treating this with boiling water the oil and pitch would collect on the surface and be skimmed off. The material was also used in later times for the remedy above mentioned. The seepage today is a pool of water covered

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<sup>8</sup> Wm. Walker: Petroleum in North Staffordshire. *Pet. Rev.* (1911) 24, 301.

<sup>9</sup> W. G. Peasegood: Discharge of an Inflammable Oil in a Coal Seam (Staffordshire). *Trans. Inst. Min. Eng.* (1909) 35, 116.

<sup>10</sup> J. P. Prestwich: Memoir on the Geology of the Coalbrookdale Coalfield. *Trans. Geol. Soc.* (1836) 5, II, 413.

<sup>11</sup> M. Elele: On Making Pitch, Tar, and Oil, out of a Blackish Stone in Shropshire. *Phil. Trans.* (1697) 19, 544.

with black oil, which is constantly collecting. The seep occurs in a small patch of pre-Cambrian on the crest of an anticline. The Carboniferous is found on all sides and covers the fold, and it was from quarries in this that the "blackish stone" was secured. In pre-Carboniferous rock, including pre-Cambrian, to the west of the Coalbrookdale coal field, tar and bitumen are found but these can usually be ascribed to the presence, either now or formerly, of Carboniferous strata. Murchison<sup>12</sup> mentions some of these and appears to confound anthracite for bitumen as he describes one place (Lyth Hill) where the "anthracite" is viscid and runs out of the cavities in the state of mineral pitch.

In the important Lancashire coal field, located 40 mi. north of the North Staffordshire district, colliery seepages are reported. The members of the Carboniferous become very thick. The coal field has some very large faults and the structural details are not well known. From here northward to Scotland, oil indications diminish, but interesting occurrences are found at Whitehaven, on the west coast, and in the Tees district, on the east coast.

Occurrences in the Mesozoic of the eastern and southern portions of the country are usually found in shallow water wells, used for domestic purposes, and as a rule are discovered during an unusually dry season when the water level is pumped down so as to bring up the contents floating on the surface; or in cases when the cover has been removed for repairing the well. The oil floating on these water surfaces is white to amber or light green in color, is mostly kerosene but usually carries such fractions as light lubricating oil, some wax, and elaterite. The writer looked into several occurrences, such as Gainsborough, Ramsey, Basingbourne and Chobham. The Ramsey oil first appeared in the winter of 1917 and continued for at least four years, during which time some thousands of gallons were collected and sold. One explanation of these seepages is that the oil represents accumulation from surface storage, affected by the alteration of years of standing perhaps. But according to the chemical work done on samples by J. E. Hackford the oil in most cases is a true petroleum with Carboniferous affinities.

The Scottish seepages are largely confined to the Carboniferous in the vicinity of Edinburgh, in which area the oil-shale fields are found. A few years ago, however, there was an important oil flow in a colliery 10 miles northeast of Glasgow and indications are reported in the Devonian of the north of Scotland. The Edinburgh seepages are in the form of hard bitumen, wax, and oil. The oil-shale measures are intruded with sills and vents and it has been the custom to ascribe these products as due to heat effects of the intrusives on the oil shales. In the oil-shale mines, the hydrocarbons are found in both igneous and sedimentary rocks and, in chemical characteristics, are closely related to those of

<sup>12</sup> Sir Roderick Murchison: "The Silurian System." London, 1839.

England. In the sediments of a pit on the flanks of the Broxburn dome, hundreds of barrels of oil with brine water were collected some years ago, and black waxy oil was collected during this work from the workings on the Pumpherston dome and at West Calder. East of the main oil-shale field is found the historic St. Catherines well, 5 miles southeast of Edinburgh in the direction of the D'Arcy well. By its size and appearance, this seepage would impress the average oil geologist at once. It is situated in Carboniferous rocks in the vicinity of a large fault separating these strata from the Devonian on the west. There is a pool of water covered with black oil and occasional rumblings of gas occur. The pool is protected by a stone house built, I believe, by one of the Stuarts, the place having been frequented in former times for medicinal treatment.

Mention should be made of the chemical correlation of the various seepage material collected during the investigation and carried out by Mr. Hackford. His chemical work checked the geological in indicating a lower Carboniferous derivation for the bulk of the material. His studies also enabled him to foretell closely the character of the crude ultimately found in drilling.

As to the significance of the various oil indications in the United Kingdom, this perhaps will not be well understood for some time to come. As some critics have maintained, are these indications of no value or do they indicate that the country as a whole is a dead oil field and past hope of ever being commercially productive? Certainly at some former periods in the history of the country, valuable deposits must have existed, and the Hardstoft well should help invalidate the view that these have all disappeared or become "insipissated." Any one acquainted with the hazards of wildcat drilling will acknowledge that eleven scattered wells are insufficient to test thoroughly a country having the size and geological conditions of the United Kingdom. The method of balancing the books by taking the difference between the cost of the prospecting to date and the return in oil sold, and writing it off as a loss is, if anything, premature. It would be more reasonable to let the balancing rest with the future, until more work may have been done.

## REGION OF THE ENGLISH WELLS

### *Geology*

The core of the Pennine Chain to the west of the Derbyshire wells is made up of outcrops of the Mountain Limestone, of lower Carboniferous age. Opposite Sheffield, the Limestone dips under the Pendleside series and does not reappear again until some 40 miles farther north, whence it continues in the range to the Scottish border, gradually changing and becoming interbedded with shales, sandstone and coal seams. In the

Derbyshire area, however, the formation is made up of at least 1500 ft. of gray limestone, usually massive and, in the upper part, locally dolomitic. The base of the formation is not here exposed. On the eastern flanks of the range, the upper horizons contain local deposits of igneous rock of basic character, consisting of intrusives, contemporaneous flows and tuffs, and to these the name "toadstone" is applied by the lead miners. The development of igneous rock in the Carboniferous of England does not begin to reach the importance it does in Scotland.

Above the Limestone is found the Limestone Shale, Yoredale, or Pendleside, as it is variously called. In Derbyshire, this formation is made up of about 400 ft. of black fissile shale with thin impure limestones, and is usually spoken of as the Yoredale or Limestone Shales. On the Staffordshire side of the range, the formation thickens greatly, develops sandy beds, and is referred to as the Pendleside.

Next in the section comes the Millstone Grits, a series of medium- to coarse-grained sandstones and grits separated by important shale members. On the east side, the thickness is about 1500 ft., while on the west side this thickness dwindles to a few hundreds of feet.

Resting on the Grits are found the Coal Measures, divided into the lower, or unproductive, and middle, or productive. Both members are largely argillaceous and sandstone beds are apt to be impersistent or wedge shaped. The lower measures are about 1200 ft. thick, the middle several times this figure. Upper coal measures, reddish in color and poor in coal, are well developed on the Staffordshire side of the Pennines; but on the eastern side they have only recently been discovered in borings, concealed beneath the Mesozoic.

The Derbyshire coal field dips eastward under cover of the Mesozoic in Nottinghamshire to form a "concealed" coal field, now being actively prospected for coal by borings and shafts. In this area, the top of the Carboniferous beneath the capping has been eroded into a remarkable peneplain, almost a geometrical plain with a length, north and south, of over 100 miles and a width of at least 30 miles, dipping 75 ft. per mile east.

### *Structure*

The core of the Pennines, where the limestone outcrops, is in the form of a broad flexed dome developed on the Pennine uplift. On the flanks of this huge structure are found subsidiary folds, on some of which on the east and west sides the locations were placed.

In the area of the limestone core, the dips are moderate, as a rule, and the regional dip in general decreases in passing eastward across the Derbyshire coal field. That is, 10° might be considered an average dip in the area of Millstone Grit outcrops, while on the east border of the exposed Derbyshire coal field the average may be closer to 2°. Locally,

however, in the coal field the dips become much steeper than this figure. On the Staffordshire side of the range, the deformation of the strata, both as to folding and faulting, is more intense than on the eastern flanks.

Faulting is an important feature in the structure of this part of England; in fact, faulting looms largely in the deformation of most parts of the British Isles. In Derbyshire, faults are of the normal type. Each square mile usually shows some sort of dislocation. The larger ones have a displacement of 100 yd. or so, and some are traceable for half a dozen miles. In this east side coal field, there is a tendency for the faults to form in two systems, one paralleling the axes of folds or the structure contours, the other intersecting these at a high angle. In the faults on the long roll running northeast from Sheffield, this type of intersection is well developed, the angle of intersection approximating  $60^\circ$ . In the Staffordshire coal field overthrusting is present, especially on the western side.

Fig. 1 shows that the folds on the west flanks of the Pennines have a general parallelism to the range, while in the less-deformed region of the east flanks this parallelism is absent, but the folds tend to radiate from a center lying west of Sheffield. There appears to have been some difference in the nature of the forces causing deformation on the two sides of the range. The generally normal-faulted condition of the east side suggests stretching of the crust with subsequent adjustments by the faults. The stretching might be due to localized radial or vertical forces acting upwards, resulting in the formation of the scattered folds and the type of faulting found. Such radial forces might arise from laccolithic action, or the subsidence of the strata along buried ridges of older rocks. The occurrence of thick toadstone deposits in the limestone of the Brimington well, and agglomerate in the core of the Ashover dome, suggests laccolithic action as the cause of some of these structures.

#### PARTICULARS OF THE ENGLISH WELLS

The well logs given are based on samples taken every 5 ft. and worked up in conjunction with the tower reports. Owing to lithological similarities, it is difficult to place the lower coal measure—Millstone Grit contact, and the Millstone Grit-Limestone Shale contact. The latter boundary is taken as the horizon where mica in the shales disappears. It will be noted that according to the correlations made there is a marked thickening of the formations northward. In the Ironville No. 1 well, the Grits have a thickness of 840 ft. and the Limestone Shales a thickness of 180 ft. At Renishaw, 16 miles north, these have increased to 1420 ft. and 660 ft., respectively. There is also a corresponding thickening of the lower coal measures. The structures, with the exception of Brimington, Ridgeway, Werrington and D'Arcy, were worked up in conjunction with information supplied by mining companies. The maps

and publications of the Geological Survey were also found of great value during the investigations.

The two Ironville wells were on the same fold, No. 2 being  $2\frac{1}{2}$  miles north of the other and several hundred feet lower on the structure. The fold is a well-defined dome, with a length of 8 miles from Langley Mills to Blackwell, and closure of 500 ft. or more. The dips vary round  $5^{\circ}$ , but on the west flank these steepen in places to  $20^{\circ}$ .

No. 1 was placed on top of the dome close to the intersection of two faults, one trending with the axis and partaking of the nature of a sharp broken flexure; the other having a displacement of 90 yd. and intersecting the first at right angles. The well started 50 ft. below the base of the productive coal measures. The Grits were reached at 983 ft., the Limestone Shales at 1840 ft., and the Limestone at 2031 ft. In the Grits at 1400 ft. was a 50-ft. sand with salt water and some black oil. At the top of the Limestone, a small showing was found yielding a barrel or so of oil of  $30^{\circ}$  Bé. At 2280 ft. (in the Limestone), a thickness of 120 ft. of toadstone was penetrated. For 600 ft. below this, occasional colors of oil with gas were noted, the hole being full of water however. At 3600–3630 ft. in the Limestone, the washed samples showed good tests for oil, 0.4 per cent. by weight. The hole was full of water from horizons above. A shot of 180 lb. of dynamite was discharged and some time spent in endeavoring to shut off the water without success, leading to the abandonment of the hole.

No. 2 started in the productive coal measures, reached the lower coal measures at 760 ft., the Grits at 1680, the Limestone Shales at 2740, and Limestone at 3029 ft.; 80 ft. of toadstone was encountered in the same position as that at No. 1, and water horizons in the Limestone of the two wells coincided fairly well. Colors of oil were found in the Grits at 2170 and 2640 ft. and at the top of the Limestone the upper 6 ft. showed colors and had a very live odor, but looked too soft to shoot.

The Hardstoft well was placed on top of a well-defined dome trending for over a mile to the northwest, and to the southeast continuing for many miles with plunging axis. The usual dips are  $5^{\circ}$  to  $10^{\circ}$  but on the southwest flank these locally reach  $20^{\circ}$ . Just west of the well, and paralleling the axis is a 50-yd. fault. The location was placed with the intention of encountering this fault where it intersected the Limestone. There were not many data available for calculating this intersection, and during the drilling there was good reason to believe that the fault zone was passed through between 1350 and 1550 ft. in depth, which would give the fault plane a dip of  $60^{\circ}$  and cause it to strike the Limestone 1000 ft. to the east. The well started in the productive coal measures, reached the lower at 444 ft., the Grits at 1533 ft. (?) the Limestone Shales at 2710 ft., and the Limestone at 3077 ft. When the well passed through the faulty zone, some colors of oil and puffs of gas occurred, with water.

On top of the Limestone, beneath a hard shell, oil was found in May, 1919, in a sandy limestone probably not exceeding 5 ft. in thickness. There was only a little gas present and it required eleven days for the oil to fill the 8-in. casing and overflow. The oil continued flowing at a very uniform rate all the time the writer was present (until the fall of 1921) and showed little decline. Two years after coming in, the well was given a pumping test, after which the oil rose to the surface in 15 days. The well was drilled 50 ft. below the sand to 3130 ft. without altering the production.

According to information supplied by H. M. Petroleum Department the production of the well has been as follows:

	U S. BBL.
May to December, 1919 . . . . .	1666
Year 1920 . . . . .	2909
Year 1921 . . . . .	2652
Year 1922 . . . . .	974

The sudden decline in 1922 is thought to be due to the necessity of cleaning out, as the oil is high in wax and the sand is protected from the overlying cavey shale only by a few lengths of perforated 6-in. liner. No attempt has been made to increase the flow by shooting or cleaning out. In character the oil resembles Pennsylvania crude in certain respects. It has a gravity of 40° Bé and analyzes by steam distillation as follows:

	PER CENT.	SPECIFIC GRAVITY	DEGREES BAUMÉ
Gasolene . . . . .	10	0.720	65
Kerosene . . . . .	30	0.7835	48
Light lubricating oil and wax . . . . .	30	0.838	37
Heavy lubricating oil . . . . .	30	0.893	27

Sulfur 0.42 per cent. Wax (melting point 104° F.) 3.25 per cent.

In 1920, when Pennsylvania oil was selling at \$6.10 per barrel, about 4000 bbl. of the Hardstoft oil were sold to relieve the storage tank for a price of £22:10:0 per ton or about \$14 per barrel at normal exchange rates.

The Heath well was located on top of an elongated dome which is an offshoot trending in a northerly direction from the Hardstoft fold, the two being connected by a saddle. A mile north of the well the axis begins to plunge and may connect with the Brimington anticline; several hundred yards east of the well is an axial fault having an east downthrow of 50 yd. The well started fairly high in the productive coal measures. The lower coal measures were reached at 1025 ft., the Grits at 2040 ft., the Limestone Shales at 3455 ft., and the Limestone at 3942 ft., the hole being carried to a depth of 4014 ft. At 264 ft. a 50,000-ft. gas flow was encountered; and at 1873 ft., near the base of the lower coal measures,



a 12-ft. sand yielding 400,000 cu. ft. per day. The latter supply was used for some months under the boilers and in the camp. Again at 2864 ft., in a 5-ft. sand between two water horizons, a 75,000-ft. flow was found. At the top of the Limestone, a small oil showing was obtained; this had a gravity of 42° Bé. and resembled a filtered variety of Hardstoft oil. The showing was shot with 400 lb. of dynamite, and later with nitroglycerine. As the laws of the country forbade the transportation of this explosive, the fluid was leached with water from dynamite on the spot. Neither of these shots was successful in increasing the showing.

The Brimington well was placed on top of a dome developed on the crest of the Brimington anticline, which has a length of 8 miles and north of the location curves into a west of north trend; lower coal measures form the crest and productive measures the flanks. At least two domes are developed on the fold, the one tested having a closure of several hundred feet. The Grits were entered at 1010 ft., the Limestone Shales at 2420 ft., and the Limestone at 2995 ft. Gas was found at 1075 ft. in the top of the Grits beneath a water sand; it was under sufficient pressure to make the water overflow and caused a subsequent collapse of 12½-in. casing. The gas contained carbon dioxide, 0.40 per cent.; methane 79.82 per cent.; and nitrogen (by difference) 19.78 per cent. Gas and oil colors were found at 1430 ft. and "wet" gas at 2215 ft. In drilling through the lower 400 ft. of Limestone Shales, colors of oil and puffs of gas were frequent, but the Limestone itself was barren except for a few positive sample tests. Toadstone was found at 3200 ft., interbedded with limestone. The toadstone beds totaled about 700 ft., between here and the bottom, 4040 ft., which was in limestone. At 3670 ft., the beds carried considerable anhydrite for 100 feet.

The Renishaw well was located on a terrace formed in the easterly dipping coal measures. The dips were under 5° as a rule, and the structure had little if any closure. The lower coal measures were reached at 584 ft., the Grits at 1950 ft., and the Limestone Shales at 3400 ft. The top of the Limestone was not sharply defined, as in the other wells. Beds of Limestone began to appear at 3978 ft. but the main mass was not reached until 4130 ft. Some oil colors were noted at 1490 ft., and at 1580 ft. a gas sand producing 200,000 ft. At 1615 ft. more gas was encountered in a sand, the total flow from the two places amounting to 750,000 cu. ft. per day. These were shut off with mud fluid. At 2020 ft. there was some "wet" gas, and at 3978 ft. a show in limestone. The lower 300 ft. of Limestone Shales yielded frequent oil colors and the tools would come up spotted with it. The final depth was 4185 ft.

The Ridgeway, or most northerly, well of the Derbyshire group was located on a large plunging fold trending south of east. A mile west of the well the axis flattened and developed some closure, while a fault giving some hundred feet of closure was present to the west of the well.

The hole started in an area of lower coal measures. The Grits were entered at 1090 ft. (?), the Limestone Shales at 2500 ft., and the Limestone at 2810 ft. A little gas was met at 475 ft. At 2888 ft. in the Limestone, sulfur water was found, which overflowed at the rate of 200 bbl. per hr. The water temperature at the top was 110° F. at first and increased in a day or two to 120° F. as the ascending water heated the strata and so lost less heat by radiation. The water had medicinal qualities and efforts were made to dispose of the find for commercial purposes. When shut in with a gate valve, the closed pressure at first registered 56 lb. per sq. in., which it maintained for three months and then gradually declined to 30 lb., around which figure it oscillated to a small degree for some time, until the well was plugged. A noteworthy feature concerning the water flow was that this entered the cellar after flowing from the casing, thence it disappeared down the hole, presumably being absorbed by the strata in the upper parts of the well. The final depth was 2996 feet.

As to the Staffordshire wells on the west side of the Pennines, the most easterly or Werrington was placed on the axis of a fold trending north for 4 miles from the well and south for a much greater distance, in the latter direction the axis having a decided pitch to the south. The location was placed on a flattening about 300 ft. below the top of the structure. There was evidence of an axial fault to the west of the well. Along the crest the structure was gentle, but on the flanks it increased rapidly in dip, which in places exceeded 40°. The Meir Hay seepage on the southwest flank has already been mentioned. The well started about 200 ft. below the Third Grit and was carried to a depth of 2670 ft. through the shales and sandy beds of the Pendleside series without finding the Limestone. The hole was abandoned on account of a fishing job. At 1850 ft., a pocket of gas was found; and at 2180 ft., gas and colors of oil.

The Apedale well was located atop a pronounced elongated dome on the west side of the coal field. The fold is 5 miles long with the well in the middle. The closure on the northeast, or weak, side is 900 ft. The crest is a broad gentle flexure but on the west flank there is a sudden pitch so that the measures dip almost vertically for 1500 ft. and then flatten abruptly, with some overthrusting at the base of the pitch in the coal workings. On the east flank, the dip is uniform, 30° to 40°. The fold is faulted, the larger displacements being several hundreds of feet; some of these are reported to increase on reaching the synclinal area on the east. One fault system crosses the axis at an angle of 45°, another crosses more at right angles, while the overthrusting on the west flanks parallels the structure. Small seepages in the vicinity have already been mentioned. A surprising and unlooked for development in this hole was the great thickness of volcanic ash encountered. This was entered

at 1450 ft. and continued to the bottom, 4248 ft., but was a very easy formation to drill. This is by far the thickest volcanic material known in the Carboniferous of England. The ash was reddish in color, basic, and rich in augite. The well started in coal measures and apparently reached the base of the Third Grit at 1050 ft. Some gas was found at 100 ft. and a few samples tested positively for oil.

## REGION OF THE SCOTTISH WELLS

### *Geology and Structure*

Fig. 2 shows, in sketch, the geology of a part of the Carboniferous basin of central Scotland, in which two wells were put down. The basin is flanked on the north and south sides by Devonian and older rocks. In its broader features, the basin is made up of a large sag forming the Glasgow coal field in the western portion, followed by an uplift to the east of this in the vicinity of Edinburgh; the latter in turn is succeeded on the east by another depression, which in its southern part is represented by the Dalkeith coal field. Adjoining the coal field on the east is the fold tested by the D'Arcy well, to the east of which the Carboniferous structure is not well known but the strata are but moderately deformed on the whole.

In this area the Carboniferous is subdivided in descending order as follows:

Coal Measures.—Sandstone, shale and coal seams.

Millstone Grits.—Sandstone and grits, thin limestone, coal.

Carboniferous Limestone Series.—Sandstone, shale and limestone, with coal seams developed in the middle portion.

Calcareous Sandstone Series, subdivided as follows:

*Oil Shale Group*.—Upper part with shales sandstone and thin limestones, carrying most of the commercial oil-shale seams; lower part contains some oil shale, several important sandstone members, and shale.

*Cementstone Group*.—Shales, sandstones, some conglomerate; Arthur's Seat and Carlton Hill volcanic zone, Fig. 2, is at the top. This group grades down into the sediments of the upper Old Red Sandstone, which however is unconformable with the lower Old Red Sandstone, which in this region contains much igneous material.

The thickness of the above section runs into thousands of feet, but that of individual members is apt to vary from place to place. Igneous material forms a notable part of the Carboniferous. This is more often of a basic character, consisting of flows, ash, sills, and isolated vents. No attempt is made to show all these in Fig. 2.

Practically all the oil shale of Scotland is mined from the formation shown, about 15 miles west of Edinburgh. Some shale was, at one time, mined on the anticline at Straiton, west of the D'Arcy well. The oil-



FIG. 2.—MAP OF GEOLOGY IN VICINITY OF EDINBURGH, SCOTLAND; COMPILED FROM GEOLOGICAL SURVEY MAPS.

shale formation rises from under the measures of the Glasgow coal field to the west and, forming a broad bench, is deformed into pronounced domes usually separated by broad synclines or relatively flat strata. The type of structure developed in the oil-shale field appears to be unique

and is confined to the area where oil shale is mined. There is perhaps some significance in this connection. There is some hint that the doming may be due to laccolithic action. Some strong faults are developed, usually normal, occasionally with a throw of 1000 ft. or more. The fault along the east side of the Pentland Hills, which is one of the major displacements of the region, is thought to be of the overthrust type. Because of the thick drift which covers the country, the details of the structure often become known only through mining operations, and mapping where surface exposures only are available is sometimes subject to radical change when the underground formations become mined.

### *Details of the Wells*

The West Calder location was placed on the summit of a pronounced dome forming the major feature on an anticline of somewhat longer axis. On three sides the dips vary up to  $25^{\circ}$ , but the south side is represented by the plunging axis of the anticline which runs south for several miles with a pitch of  $6^{\circ}$ . The boring started in the upper oil-shale group and several oil-shale seams were found in the upper part of the hole. These drill like leather. Oil colors were of frequent occurrence down to a depth of 1200 ft., and at 815 ft. a 10-ft. sand showed heavy oil, enough to give the tools a thick coat whenever passing through. At 945 ft. was a 50,000-ft. gas sand. It had been expected that several sandstone members known to occur in the lower part of the oil-shale group would be picked up before a depth of 2700 ft. was reached, but between 1680 and 2980 ft. there was an almost continuous mass of ash or agglomerate with some solid igneous, all basic in character. A shale break 100 ft. thick occurred at 2500 ft. The occurrence of this ash was unexpected and, so far as the writer is aware, no correlation has been made of this nor the sediments below, which may still be the oil-shale group. Below the ash to the bottom (3918 ft.) were shales with some ash streaks, some full of lime. The first appreciable water below 1500 ft. was found at a depth of 3909 ft. and beneath this were showings of oil and gas with the hole full of water. Some oil colors were noted at 2607 ft. beneath the shale break, and also at 3394, 3488, and 3705 ft. The well was abandoned because of bad hole.

The D'Arcy well was on a broad moderately folded anticline adjoining the Dalkeith coal field on the east. The fold has a northward trend and is over 8 miles long. Several domes are developed on the structure, the location being on the most important. The Carboniferous limestone series forms the surface. The oil-shale measures underlying this have never been prospected on the fold except by the present boring. In the well, the oil-shale group was entered at a depth of 200 ft. and several seams were found. At 724 ft. gas was found in a sand; and when measured with the hole partly filled with water and cavings tested 300,000 cu. ft.

per day. The gas contained methane and ethane 76 per cent.; nitrogen 24 per cent. At 905 ft., some heavy oil was found in association with water in a sand. At a depth of 1810 ft., an encouraging show of oil was found but the well had to be stopped on account of drilling difficulties. This was after the departure of the writer, but he is informed that the oil is of high grade, resembles that at Hardstoft, and over 50 bbl. were bailed out. The well is reported standing pending arrangements with private interests to undertake further work.

#### VARIATION IN FIXED CARBON CONTENT OF COAL

During the early stages of the geological work, White's paper on the relation of the fixed carbon percentage in coal to the Appalachian oil and gas fields appeared, and in consequence all available proximate analyses of British coal were secured with the view of applying his results to the problem in hand. Most of the analyses obtained were for commercial purposes and usually gave no hint as to the method of analysis employed. The data available, therefore, were not as satisfactory as could be desired, as proximate analyses do not, as a rule, check unless made by the same method and various methods were in vogue in the data obtained. In a general way, these analyses gave as an average for Derbyshire coal a fixed carbon content of 60 per cent. (this figure is herein calculated on the ash- and moisture-free basis), and the same figure seemed to suit the coals of Staffordshire and the Edinburgh area. In the southwest of the country, in the South Wales coal field, the figure was higher, and also in the north of England, in the Durham coal field, where the coal usually went 70 per cent. fixed carbon or better.

But although 60 per cent. was an average, there was considerable variation in the same section and even in the same seam. Thus the lowest workable coal in Derbyshire in the lower coal measures, the Kilburn, was reported by one colliery to run 55.7 per cent. fixed carbon, while the Top Hard seam in the same district, 1500 ft. higher in the section, gave figures as high as 63 per cent. Again, cannel portions of the Top Hard were as low as 50 per cent. Accordingly, during the progress of the drilling, the writer secured various coal samples from mines and had them uniformly analyzed by the American method. In the vicinity of the Hardstoft well, the Blackshale coal at the base of the productive coal measures gave 59.1 per cent. fixed carbon. The Low Main seam, 200 ft. above, went 62.7 per cent.; and the Deep Hard, 450 ft. above, 64.7 per cent.; that is, the fixed carbon content decreased with depth. Near the Heath well, the Blackshale coal at a depth of 1000 ft. went 64.4 per cent. fixed carbon, while a few miles east at a depth of 2000 ft. the figure was 59.5 per cent.; but at the latter place the seam was of a cannel variety.

With regard to the variation of percentage in the same seam, samples of commercial grades from the Barnsley, the Top Hard equivalent, from

a mine a few miles northeast of Sheffield, were made by the above method with the following results: Cannel, 56.2 per cent.; softs, 63.2 per cent.; hards, 64.4 per cent. fixed carbon.

As to variation arising from the method of analyses, such as would be liable to enter data of the nature collected, a sample from a coal seam in one of the oil-shale pits at West Calder gave by the American method 51.0 per cent. fixed carbon. An analysis of the seam by the company, using its method, gave 57.5 per cent. An analysis by the same company of the Hurler coal, much higher in the section, yielded 61.2 per cent. fixed carbon.

The foregoing figures would indicate that caution is needed in using the fixed carbon content of coal as a means of determining the oil prospects of a region, especially if this happens to be a new one or foreign. The assumption made by some, in using coal analyses for this purpose, that the fixed carbon content increases with depth is not borne out by the figures given. The question arises as to how much of the variation of the fixed carbon content is due to metamorphism, and how much to differences in the original character of the coal itself.

#### WELL TEMPERATURES

Thermometer readings were taken at various depths during the drilling of the wells, whenever a suitable opportunity presented itself. It was not always easy to find a well in suitable shape to take a reading, as the action of the bit had the effect of heating the strata, the heat effects being in evidence sometimes for several days. In conjunction with the Mine Temperature Research, Doncaster Coalowners Laboratory, brass cases were designed with spring mountings to hold the thermometers, which were of clinical type. Two cases were used, one inside the other, the object of these and the springs being to lessen the effects of jar in raising and lowering the apparatus on the tools, and to obviate water-pressure effects on the mercury bulb of the thermometers. The thermometers, in batteries of two or three, were usually tied to the top of the bailer and left in the hole for 2 hours.

The presence of casing in the hole did not appear to affect the results, neither did the presence of water in the hole so long as it was not flowing over the top. It should be mentioned that at Ironville No. 1, water was struck at 2417 ft. and overflowed at the rate of 10 bbl. per day. The water on issuing from the top was cool, of air temperatures. This gave the impression that the water horizon was also cool, but a reading at the bottom of the hole showed a temperature of 103° F. indicating that the water was cooled in its slow ascent in the hole. These results indicate little or no effects from convection currents in the sizes of hole used. In the case of strong flows, as at Ridgeway, the water ascended too rapidly to be cooled by the walls.

The results show that the temperature gradient is not uniform in the same hole, nor do the same horizons in the various wells show the same gradient. This indicates that the isothermal surfaces are not planes, but curved or sinuous surfaces. This condition must be caused by unequal conductivity of the strata of a marked order, or else the local production (and absorption) of heat in the strata by chemical action, radioactivity, crustal strain, and similar phenomena. Perhaps both causes influence the gradients. At times the existence of "sources" and "sinks" of heat were suspected from the anomalous results obtained, but the nature of the experiments was such that no reliance could be given the suspicions.

The more reliable readings are given in the table. The strata in Derbyshire at a given depth are, on the average, hotter than those at the

TABLE 1.—*Well Temperatures*

Well	Depth, feet	Temperature, Degrees, F.	Remarks
Ironville 1.....	2400	103.0	Hole full of water
	3555	123.5	Hole full of water
Ironville 2.....	1960	89.6	
	3075	119.0	Hole full of water
	3530	127.0	2700 ft. water in hole
Hardstoft.....	2977	103.0	
Heath.....	3200	107.5	
	3660	122.0	
	3975	124.0	
Brimington.....	2460	100.0	
	3000	117.5	24 hr. after drilling
	3990	121.5	Hole full of water
Renishaw.....	1725	87.0	400 ft. water in hole
	2720	104.0	200 ft. water in hole
	3635	119.0	250 ft. water in hole
Werrington.....	1815	71.0	
	2210	80.0	350 ft. water in hole
Apedale.....	1715	74.5	
	3200	95.5	
	4230	113.0	1500 ft. water in hole
West Calder.....	2160	79.0	250 ft. water in hole
	2950	89.0	
	3870	114.5	3200 ft. water in hole



TABLE '2.—*Water Analyses*

Well.....	Mountain Limestone			Millstone Grits			Lower Coal Measures		Igneous	Oil-shale Group	
	Iron-ville 1 2462 Middle	Brim-ington 4040 Lower	Reni-shaw 4185 Upper	Iron-ville 1 1433 Middle	Reni-shaw 3198 Lower	Ridge-way 1115 Upper	Hard-stoft 902 Middle	Reni-shaw 1670 Lower		West Calder 3910 Lower	D'Arcy 905 Upper
Specific gravity at 60° F.	1.003	1.116	1.116	1.014	1.127	1.60	1.010	1.009	1.1775	1.063	1.004
Constituents reported in.	<sup>a</sup>	<sup>a</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>a</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>a</sup>
Calcium.....	16.40	54.34	13.85	0.26	15.20	1.60	0.188	0.24	35.97	4.85	10.12
Strontium.....	0.34	1.16	0.36	0.017	0.67		0.0025	tr.	0.50	0.88	0.46
Barium.....				0.005	0.93					0.48	0.41
Magnesium.....	4.92	9.81	2.96	0.11	2.30	0.30	0.051	0.075	0.12	1.49	3.57
Sodium.....	9.17	38.82	37.40	6.64	40.45	47.84	4.88	4.25	42.33	24.62	181.31
Potassium.....	0.68	tr.	0.29	0.061	0.15	1.28	0.08	0.046	0.27	0.20	1.46
Lithium.....	0.06	tr.	tr.	0.002		tr.		tr.	0.007	tr.	tr.
Ammonia (NH <sub>4</sub> ).....	0.095	0.085	0.11	0.0014	0.085	0.01	0.0075	0.0051	0.012	0.06	0.81
Iron.....	0.05		0.05		0.023			tr.			
Aluminum.....					0.009						
Manganese.....					0.016						
Zinc.....		tr.									
Chlorine.....	15.04	70.10	90.61	10.78	98.40	20.55	7.88	7.07	131.55	50.70	272.83
Bromine.....		tr.	0.86	0.056	0.965		0.077	0.041	0.76	0.62	2.90
Iodine.....			0.006		tr.				0.004		
Carbonate (CO <sub>2</sub> ).....	8.10	7.70	0.016	0.30		39.30	0.18	0.12		0.04	23.70
Sulfate (SO <sub>4</sub> ).....	46.23	138.14	0.45	0.012		11.69	0.025	0.12	0.27		5.20
Silica.....	0.16	2.40	0.002	0.012	0.002	0.96	0.002	0.006	tr.		0.40
Nitrate.....						2.20					

<sup>a</sup> Parts per 100,000. <sup>b</sup> Grams per 1000 gm.

same depth in Staffordshire and Scotland. The average gradient for Derbyshire would be in the neighborhood of  $1^{\circ}$  in 50 ft., after allowing  $50^{\circ}$  F. as the fixed surface temperature.

### WATER ANALYSES

The water horizons encountered in the wells were in most cases sampled and analyzed in detail at the Government Laboratory, Strand. No fresh water was found except close to the surface. All the waters found in deeper drilling were mineral in character, and of varied concentration, the highest specific gravity being 1.1775. The water from Renishaw at a depth of 3198 ft. was radioactive, of an order 1 in 10,000,000, and that at Hardstoft also, at a depth of 902 ft., but to a less extent, 1 in 300,000,000.

The waters, in Derbyshire, from a given formation usually differed in chemical characteristics from the waters of another formation. The Limestone waters are charged with sulfates, together with chlorides and some carbonates. Exceptions to this were brine waters from the upper limestone at about the same horizon, at Renishaw and Ironville No. 1, which carry only small amounts of sulfate and carbonate.

Except those of the top, the Millstone Grit waters were charged with sodium chloride, with sulfates and carbonates absent or in small proportions. Barium and bromine are usually present, and some show barium in solution in the presence of the sulfate radicle. This feature was carefully checked, and ascribed as due to the presence of magnesium chloride and bicarbonates holding the barium sulfate in solution. The upper Millstone Grit waters have resemblances to those of the coal measures, which carry appreciable proportions of sulfates and carbonates in addition to chlorides.

The deep West Calder water has resemblances to those of the Millstone Grits. Table 2 shows some of the representative analyses. The results are reported in two ways. To reduce one to the other multiply grams per 1000 gm. by 100.34 to obtain parts per 100,000.

## Smackover Oil Field, Ouachita and Union Counties, Ark.\*

BY H. G. SCHNEIDER,† SHREVEPORT, LA.

(New York Meeting, February, 1924)

THE Smackover oil and gas field lies in Ouachita and Union Counties, Ark., in the south-central part of the state, in T.15 and 16S., R.15, 16, and 17W. It is 10 miles north of El Dorado, the principal business and railroad center in the south-central part of the state, and extends from the town of Smackover in all directions. Productive territory having an aggregate area of nearly 55 sq. mi. has been developed. It extends 6 miles from north to south and 12 miles from east to west. The field may be divided into two parts: the east district, which includes the area east of the town of Smackover, and the west district, which includes the area west of the town of Smackover. In relation to the neighboring productive fields of Arkansas, the Smackover field is 9 miles north of the El Dorado oil and gas field, 8 miles slightly west of north of the East El Dorado oil and gas field, and 16 miles east of the Stephens oil field.

Smackover was discovered in May, 1922, when the Oil Operators Trust drilled well No. 1 on the J. T. Murphy farm, in the southeast quarter of sec. 8, T.16S., R.15W. This well is located almost on the top of the Norphlet dome and was drilled to the Nacatoch sand. It had an initial open flow volume of 30,000,000 cu. ft. of dry gas per day, and a rock pressure of 950 lb. per sq. in. In July, 1922, the V. K. F. Co. completed the first oil well in sec. 29, T.15S., R.15W., on the north side of the Norphlet dome, and 3 miles north of the first gas well. This well started the active development of the north and northwest sides of the dome.<sup>1</sup>

The field was extended westwards, when oil was discovered in the Nacatoch sand, during October, 1922, in sec. 4, T.16S., R.16W., 5½ miles west of the original gas well. This opened up the so-called "light oil district," which is located on a structural terrace, for which the name

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<sup>1</sup> H. W. Bell, P. S. Haury and R. B. Kelly: Preliminary Report on the Eastern Part of the Smackover, Arkansas, Oil and Gas Field. Arkansas State Bureau of Mines. 1923.

Louann terrace is proposed. Further development in the area surrounding this well was disappointing as most of the wells were either dry or small producers. This led to the deepening of some wells, and the finding of two producing horizons below the Nacatoch.

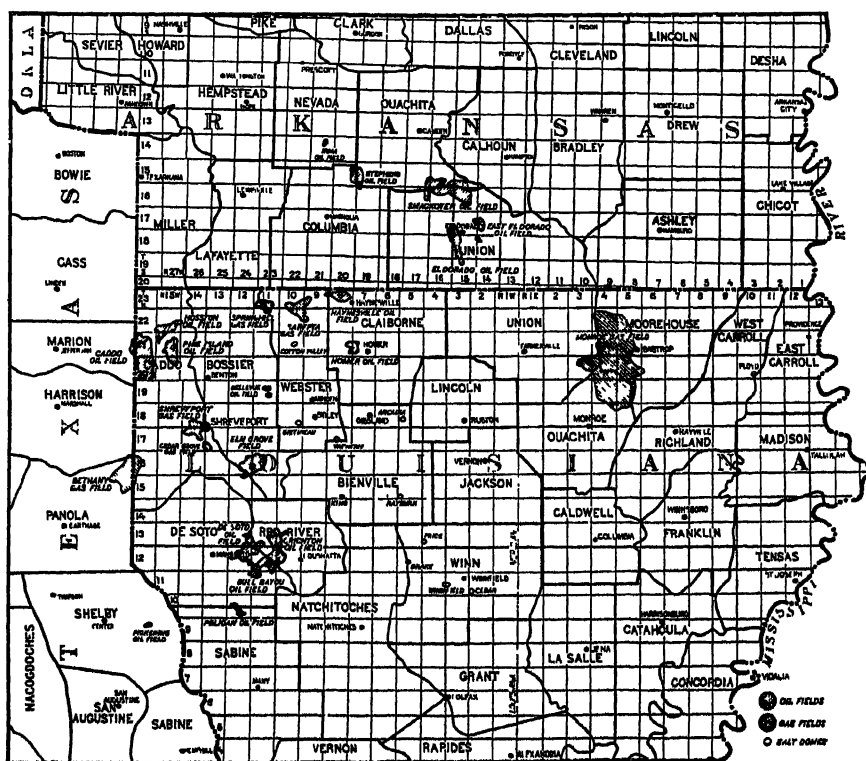


FIG. 1.—INDEX MAP OF EAST TEXAS, NORTH LOUISIANA, AND SOUTH ARKANSAS.

During the next four months, drilling was chiefly confined to proved areas, but in February, 1923, the district was extended in several directions. The Burton pool, on the northwest side of the Smackover district, was opened when a 25,000-bbl. well was completed in sec. 28, T.15S., R.16W., extending the field to the northwest. A 10,000-bbl. well in sec. 10, T.16S., R.16W. opened up the Broderick and Calvert pool and extended the field to the southwest. During this month, an oil well was completed on the south side of the Norphlet dome in sec. 16, T.16S., R.15W., and in March, 1923, the completion of a large well in sec. 10, T.16S., R.15W., on the east side of the dome, started the development of the Norphlet area.

Subsequent drilling has connected the various productive parts of the Norphlet dome and the prolific area has been well defined by dry holes; however, no wells have been drilled that thoroughly tested the

deeper horizons. In the western part of the Smackover district, producing areas have been well defined, with the exception of the area to the northwest, by dry holes.

### STRATIGRAPHY

The stratigraphy of southern Arkansas, in comparison to that of most regions of gently dipping sedimentary rocks, is obscure, the various formations being difficult to differentiate. Variations in lithology and thickness of the different formations makes their correlation in well records difficult and, in most cases, impossible. With rotary drilling, accurate logs are difficult to obtain even though samples are secured from the drilling wells, for cuttings are always mixed with fragments from the formations already passed through. Logs made by drillers without reference to samples are simply a record of the relative hardness of the formations.

### *Coastal Plain Belt of Southern Arkansas*

The southern part of Arkansas that lies in the coastal plain is underlain by strata of Tertiary and Cretaceous age resting upon a basement of steeply folded Pennsylvanian sediments peneplained prior to Cretaceous time and subsequently tilted slightly coastward. About 50 miles north of the Smackover field, The Paleozoic rocks are sepa-

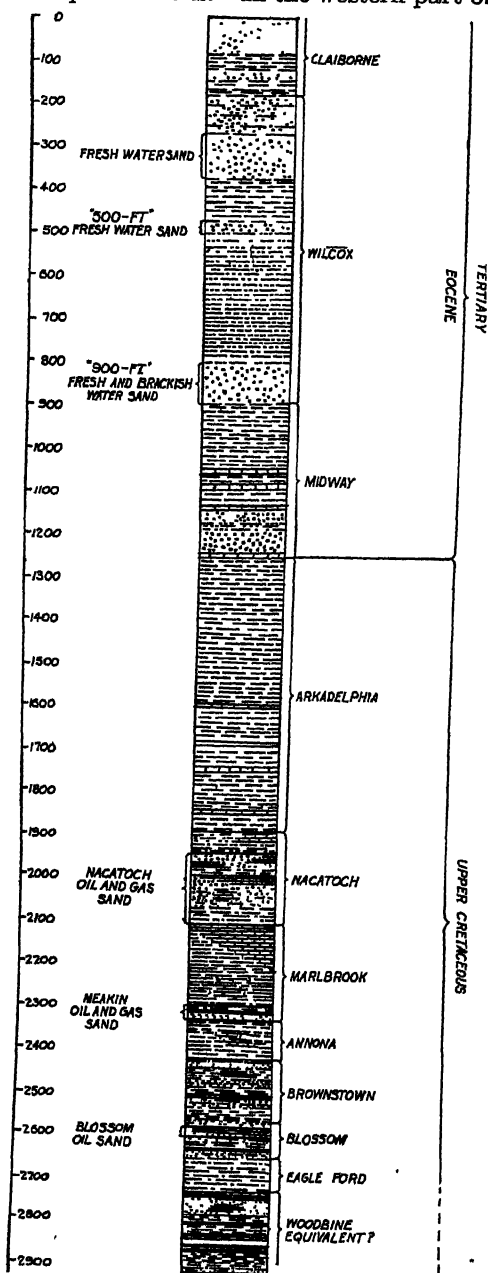


FIG. 2.—STRATIGRAPHIC SECTION OF SMACKOVER DISTRICT.

these older rocks come to the surface.

rated from the Cretaceous deposits by an unconformity including, at least, the Triassic and Jurassic and, probably, part of the Lower Cretaceous epoch. The Cretaceous deposits are divisible into two series, the Upper and the Lower. The nature of the contact separating these two has not been determined, but it may be that of unconformity, with the basal formation of the Upper Cretaceous, the Woodbine, having been deposited in the waters of a transgressing sea.<sup>2</sup> With the exception of the two basal formations, the Trinity of the Lower Cretaceous series and the Woodbine of the Upper Cretaceous series, both of which represent

## STRATIGRAPHIC COLUMNAR SECTION OF THE SMACKOVER FIELD

SYSTEM	SERIES	FORMATION AND GROUP	THICKNESS, IN FEET	CHARACTER AS RECORDED FROM WELL CUTTINGS
Quaternary	Recent			Flood-plain deposits and terrace remnants.
Tertiary	Eocene	Claiborne		Lignitiferous sand and clays and ferruginous sandy clays. Glauconitic sand common. Fresh-water sands.
		Wilcox	700	Sands, sandy clays, and shales. Some boulders and lignite. Fresh and brackish water sands.
		Midway	340	Sand, gumbo and shale with more or less calcareous materials.
Cretaceous	Upper Cretaceous	Arkadelphia	625	Dark clays, shales with calcareous material.
		Nacatoch	210	Sand, sandy shales and layers of calcareous quartzitic sandstone.
Cretaceous	Upper Cretaceous	Marlbrook	220	Calcareous clays, marly limestone and sand.
		Annona	90	Calcareous shale, some sand.
		Brownstown	145	Blue shale and sand.
		Blossom	80	Sands, sandy lime and shale.
		Eagle Ford	150	Shale, in part sandy.
		Woodbine equivalent (?)	200 (?)	Red shale and gumbo, limestones, and sandy shales.
	Lower Cretaceous			Limestones, shale and sand (?)

<sup>2</sup>L. W. Stephenson: Cretaceous-Eocene Contact in the Atlantic and Gulf Coastal Plain. U. S. Geol. Survey *Prof. Paper* 90 (1915) 155-182.

deposits laid down in deltas and marginal marine waters, all of the Cretaceous deposits are of marine origin. The Upper Cretaceous is disconformably overlain by the Eocene. This unconformity is a paleontological rather than a structural break. The basal formation of the Eocene, the Midway, is of marine origin, and the younger formations represent sediments deposited under littoral or palustrine conditions.

Surface rocks in the Smackover field belong to the Claiborne group of Tertiary age, and consist mainly of clays, sands, sandy clays, and lignites. These beds are covered to a great extent by surficial deposits of Quaternary age consisting of flood-plain deposits and terrace remnants. The older formations are known from well records only. In the following discussion, descriptions of the different formations are given and tentative correlations with known beds are suggested as far as possible.

### TERTIARY SYSTEM

#### *Claiborne Group*

The Claiborne group consisting of an upper and lower member, the Cockfield and St. Maurice, respectively, is present through the field and more or less weathered exposures are found over about half of it. The members consist of alternating beds of sand and clay, with boulders. The clays are thinly laminated, white to chocolate in color, and contain in a few localities thin layers of lignitiferous material. Some of the sands contain considerable glauconite, weathered surfaces of which are usually brick red in color because of the oxidation of the iron content. The St. Maurice formation has been identified on the north side of the field at Walnut Bluff, in the south part of T. 15S., R. 16W., by Harris.<sup>3</sup> Berry has identified the surface formation in the north part of T. 17S., R. 15W., on the south side of the Smackover district as being of Cockfield age.<sup>4</sup>

#### *Wilcox Formation*

The Wilcox formation consists of fine to coarse sands and gravel with minor amounts of sandy clay and shale. Limestone boulders, with varying thicknesses up to about 5 ft., are common and occasionally lignite is logged. The color varies from a yellowish brown to white. The Wilcox is usually distinguished from the Claiborne by the greater amount of sand it contains.

#### *Midway Formation*

The strata that have been assigned to the Midway in the Smackover field consist of shales and clays near the top, and sandy layers containing

<sup>3</sup> G. D. Harris: Oil and Gas in Louisiana. U. S. Geol. Survey Bull. 429 (1910) 120.

<sup>4</sup> El Dorado, Arkansas, Oil and Gas Field. Arkansas Bureau of Mines (1922) 79.

some lime near the bottom. The Midway beds are marine sediments, bluish black and light yellow in color, frequently micaceous. The Midway is distinguished from the overlying Wilcox formation, by the relative scarcity of sand.

## UPPER CRETACEOUS SYSTEM

### *Arkadelphia Formation*

The Arkadelphia formation, about 650 ft. thick, is logged as bluish-black shale and gumbo with many thin limestone layers. It is easily distinguished because of the thickness of shale without sand. The thin limestones recorded are not true beds, but are boulders; and they are confined to the lower 200 ft. of the formation.

### *Nacatoch Formation*

This formation consists of various amounts of sand, shale, gumbo, and impure limestone which have a total thickness of about 200 ft. The main producing horizons in the Smackover district are in this formation. The top of the formation,<sup>5</sup> is marked by an argillaceous limestone, which is easily distinguishable from the overlying shales and gumbos. The Nacatoch, in the eastern part of the district, is composed essentially of sand with intercalated shales and gumbos; and in the western part of the field, it consists of shales and gumbos containing lenses of sand. The decrease of sand content from the eastern part towards the western part of the field is gradual.

The sand is composed of about 95 per cent. quartz grains and about 5 per cent. glauconite grains; it is fine grained and greenish gray to gray. Induration of portions of this sand have been caused by the deposition of secondary calcite, probably from circulating underground waters.

### *Marlbrook Formation*

The 225 ft. of sediments that have been assigned to this formation consist of light gray argillaceous limestone, bluish-black shale, and fine-grained white sand. The top has not been accurately determined, but is thought to be the contact of the sand beds above and the argillaceous limestone below. In the lower part of this formation there is about 18 ft. of sand that produces oil and gas. The base, also, has not been definitely determined but fossils found in the oil-producing horizon have been identified as Marlbrook; as no fossils of this age have been recognized below this horizon, it is considered to be the base.

<sup>5</sup> Determination by A. L. Selig, Paleontologist, Atlantic Oil Producing Co., Shreveport, La.



*Annona Chalk*

Underlying the Marlbrook formation, at the outcrop, is the Annona tongue of the Austin chalk. It has not been identified with certainty in this part of Arkansas, as the well logs show no interval that is entirely comparable with the Annona at the outcrop. However, as this tongue of Austin chalk varies from typical chalk to calcareous clay, it is probably present in Union County, but because of this lithologic variation it may not be easily distinguished from the overlying formation.<sup>6</sup> The upper boundary is provisionally drawn at the upper surface of a persistent calcareous shale bed. The Annona as thus identified consists of dark gray calcareous shale containing a small amount of sand; the thickness is about 900 feet.

*Brownstown Formation*

A group of beds about 145 ft. thick is tentatively correlated with the Brownstown formation.<sup>7</sup> It is composed of sand, shale, and sandy shale, all of which is more or less calcareous. The sand beds are uniform in thickness, fine-grained, and light gray; the shale is bluish black

*Blossom Formation*

The horizon called the Blossom, in this field, consists of 75 ft. of sand, sandy shale, calcareous sandstone, and shale. The sand varies from gray to green and in places is very micaceous. The Blossom oil sand, locally called the "2600-ft." sand, is a member of this formation.

*Eagle Ford and Woodbine Formations*

The Eagle Ford and Woodbine formations may be described together as there is much uncertainty regarding their separate identities. There may be as much as 600 ft. of limey shales and clays between the Blossom sand and the Woodbine.<sup>8</sup> These three formations, Blossom, Eagle Ford, and Woodbine, have been grouped together as the Bingen formation in southwestern Arkansas, because in Little River County the Eagle Ford formation has thinned out and the Bingen sand is the combined thickness of the Blossom and Woodbine formations. In the Smackover area, however, the Blossom and Eagle Ford have been recognized and the underlying sand containing lignite is strongly suggestive of Woodbine.<sup>9</sup>

The Eagle Ford formation is composed of black gummy shale, and is about 95 ft. thick. The Woodbine sand which underlies this shale,

<sup>6</sup> Oil from the Nacatoch Sand, El Dorado, Arkansas. U. S. Geol. Survey, *Press Notice* (Feb. 7, 1922).

<sup>7</sup> Personal communication from A. L. Selig.

<sup>8</sup> J. P. D. Hull: Notes on the Stratigraphy of Producing Sands in Northern Louisiana and Southern Arkansas. *Am. Assn. Pet. Geol. Bull.* (1923) 7, 366-367.

<sup>9</sup> *Idem.*, 368.

about 55 ft. in thickness, is fine grained, dark gray to brown, and is usually very hard, due to consolidation of the beds by calcareous cement. This horizon produces oil in the El Dorado field. Beneath this sand there is about 150 ft. of beds logged as limestones and red and blue gumboes and shales, which are here correlated with the Woodbine, because red shales and clays have been noted along the outcrop at the base of the Bingen formation.<sup>10</sup>

### *Lower Cretaceous System*

Not much is known regarding the Lower Cretaceous formations in this part of Arkansas, and only one well, the Humphreys Oil Co., Massey No. 1, in sec. 17, T.16S., R.15W., which has drilled to a depth of 3480 ft. has probably penetrated them.

### THE PRODUCTIVE SANDS

The oil and gas in the Smackover district are produced from three sands—the Nacatoch, Meakin, and Blossom.

#### *The Nacatoch Sand*

The Nacatoch horizon contains the most important producing sands in the Smackover district and is 150 ft. thick, consisting of variable amounts of sand intercalated with shale and gumbo. In general, the amount of sand is greater and more consistent in the eastern part of the field; while in the western part the horizon consists mainly of shale and gumbo, in which there are scattered lenses of sand. Because of differences in texture and porosity of the sand, the content of oil, gas, and salt water is quite variable in different wells. The entire thickness of sand found in a well is seldom productive; parts of it may be dry while other parts may contain gas or oil and gas under tremendous pressure or salt water. These "streaks" or "pockets" are separated from one another mainly by layers of quartzitic calcareous sandstone, called "cap rock" by the drillers, and to a minor extent by the intercalated gumboes and shales. An examination of the calcareous material shows it is mainly of secondary origin and probably deposited by circulating underground water. Deposition of carbonates along the circulation channels probably caused the formation of a network structure that divided the porous sand beds into "pockets" of sand, some of which are connecting. Notwithstanding these impervious barriers, this sand has been immensely productive, but the yield is not nearly so great as one would expect from a sand bed of this thickness. The total oil and gas area in the Nacatoch sand in the Smackover field is about 42 sq. mi., of which about 2 sq. mi. contain gas only. The gravity of the oil obtained from this sand varies from 19° to 26° B<sub>é</sub>.

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<sup>10</sup> H. D. Miser and A. H. Purdue: Asphalt Deposits and Oil Conditions in Southwestern Arkansas. U. S. Geol. Survey Bull. 691 (1919) 282-291.

### *The Meakin Sand*

This sand has previously been known by various names, such as the "2200-ft." or "2300-ft." sand, and the "light oil" sand. The name Meakin is proposed for this sand, from the name of the farm on which the first producing well was drilled.

The Meakin sand lies about 360 ft. below the Nacatoch formation, and is found at an average depth of 2280 ft. It is productive of oil in the northwest part of the Smackover district, and is productive of gas in the vicinity of Kenova. The sand is about 18 ft. thick, and consists of fine-grained sand, comparatively hard, and uniform in texture and porosity. The cap rock, from 2 to 6 ft. thick, is extremely hard. In some localities, a soft white sand is found overlying the Meakin with a maximum thickness of about 10 ft., and in it good shows of oil and gas are found. About 8 sq. mi. produce oil and gas from the Meakin sand in the Smackover district. The gravity of the oil is about 26° Bé.

### *The Blossom Sand*

About 620 ft. below the Nacatoch is the Blossom sand, from which oil has been produced in the western part of the Smackover district. It is about 10 ft. thick and consists of fine-grained, glauconitic, micaceous sand, and in color varies from dark gray to green. The texture is quite uniform, but the porosity is variable; the hardness varies with the porosity. The area, where this sand is productive, covers about 1 sq. mi. The gravity of the oil is 17° to 20° Bé. Underlying this sand is about 45 ft. of shale containing thin streaks of sand, usually a few inches in thickness, some of which are saturated with oil, but up to October, 1923, only one commercial well had been completed in this stratum.

## STRUCTURE OF SMACKOVER FIELD

Structural conditions in southern Arkansas can scarcely be determined from surface exposures, because of the broad mantle of surficial deposits, the lack of consolidation, the crossbedding and the deep weathering of the Tertiary sediments. Exposures in the field itself are infrequent, owing especially to the central position of Smackover Creek; and only two or three exposures are thought to be reliable. These show that the strata dip south in the southeastern part of sec. 8, T.16S., R.15W., and dip northeast in the southeastern part of sec. 22, T.15W., R.15W., and dip northward in the western part of sec. 25, T.15W., R.16W.

The contours of the subsurface map, Fig. 3, are based on the top of the Nacatoch oil and gas horizon. The structure of the eastern part of the field was obtained by taking sand records of the Nacatoch sand which vary greatly over short distances because of inaccurate logs made by

the rotary method of drilling; and because of the varied lithologic character of the Nacatoch. The calculations made from the individual logs were checked with those adjacent wells; if a log was different than the

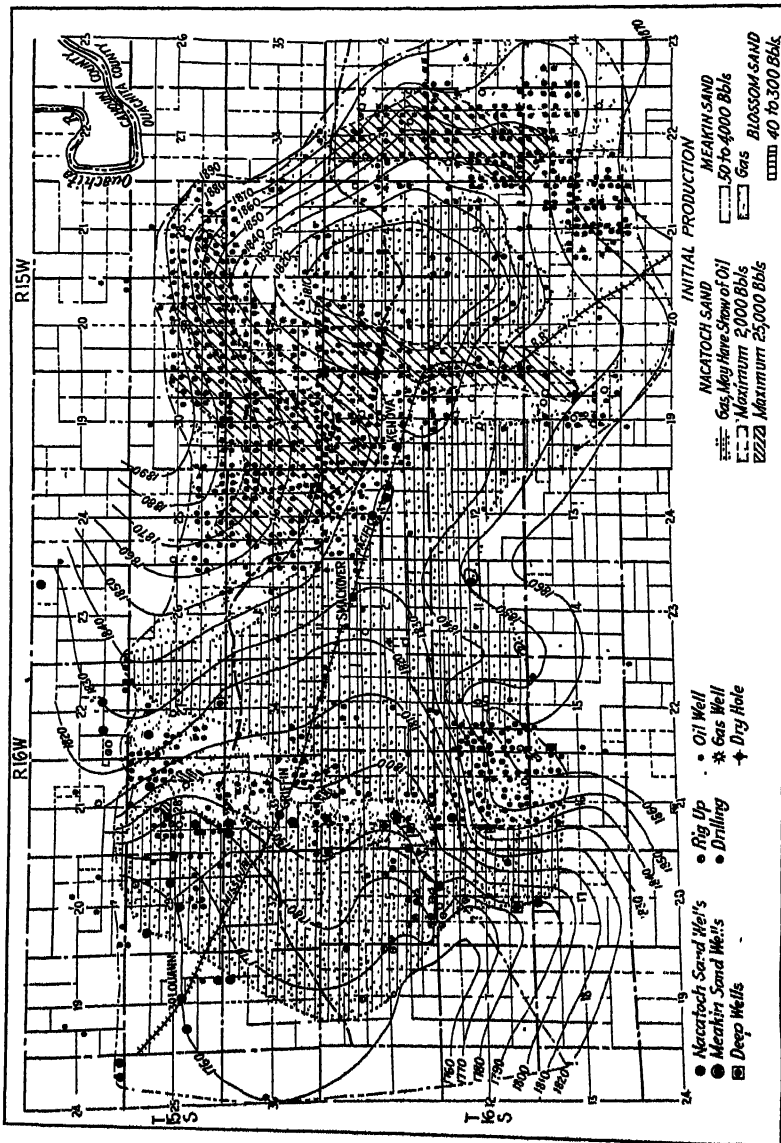


FIG. 3.—SMACKOVER FIELD.

majority of the adjacent logs, it was eliminated as inaccurate. A map, made under such conditions, is more or less generalized. The lithologic changes in the Nacatoch were noted, as far as it was possible, by means of cross-sections.

Contours in the western part of the district were determined by taking the depths of the Meakin sand and interpolating back to the top of the Nacatoch oil and gas horizon. This was done because of the argillaceous character of the Nacatoch formation over a greater portion of this district, which makes it impossible to follow any one horizon.

The major structural feature of the Smackover district is a broad, low nose about 13 miles long and 5 miles wide, the axis of which extends in an easterly direction from the southeast part of T.15S., R.17W., to the east central part of T.16S., R.15W. The sides dip to the northeast and southeast into synclinal areas. The axis of the syncline on the northern flank lies about 3 miles north of the anticlinal axis, and the axis of the syncline on the south lies about 6 miles south of the anticlinal axis. Superimposed on the east end of the fold is the Norphlet dome, the long axis of which trends slightly east of north at right angles to the trend of the major fold. West of this dome the folding becomes more irregular and consists of a prominent terrace, the Louann terrace—named after the town of Louann, which is bordered by several minor undulations. Separating the Norphlet dome from the Louann terrace is a large structural saddle, which is named the Kenova saddle. The Nacatoch exhibits some minor irregularities that are apparently not reflected in the two lower sands. This difference is usually caused by sand lensing and the top of the dome usually coincides with the thickest part of the lense. In spite of these irregularities the general structure of all three sands are considered to be the same.

#### NORPHLET DOME

The Norphlet dome is the largest feature in the Smackover field, occupying about 25 sq. mi. The top of the dome occupies the south part of secs. 4 and 5, and the north part of secs. 8 and 9, T.16S., R.15W. The dips on all sides of the dome are gentle but are steepest on the north and northeast sides, amounting to about 35 ft. per mi. The beds on the east side dip about 30 ft. per mi. and on the south side dip about 20 ft. per mi. The dip on the west side is only 18 ft. per mi. The elevation of the apex, referred to the top of the Nacatoch productive horizon, is about 1800 ft. below sea level. The closure amounts to about 35 ft. The Nacatoch is the only sand productive of oil on this dome, in October, 1923.

#### KENOVA SADDLE

The Kenova saddle lies between the Norphlet dome and the Louann terrace. The axis is, in general, parallel to the long axis of the Norphlet dome, and extends, from the southwest part of sec. 13, T.16S., R.16W., in a northerly direction to the west part of sec. 30, T.15S., R.15W.

The Nacatoch is a large producer of oil and gas on the north part of the saddle and produces gas with a small amount of oil on the top and

south parts. The Meakin sand contains dry gas on the middle part and the Blossom sand is productive on the south portion of this structure.

#### LOUANN TERRACE

In the western part of the field, the Louann terrace occupies the western half of T.15-16S., and the eastern half of T.15-16S., R.17W. It resolves itself to the west and northwest into the rising formations of the south and southeast dipping monocline. The beds of the terrace are not horizontal but pitch in a general direction toward the east, increasing from a slope of about 10 ft. per mi. in R.17W., to a slope of about 20 ft. per mi. in the east part of R.16W. The north and northeast sides of the terrace are bordered by the syncline that lies along the north side of the Smackover district, while the east side is terminated by the Kenova saddle, and the south side is bordered by the steeply dipping slope that characterizes this portion of the Smackover structure. All three of the sands are producers on the Louann terrace.

A minor terrace exists in the western part of T.16S., R.16W., the axis of which extends from the southwest quarter of sec. 6, T.16S., R.15W., southeastward to the center of sec. 21, T.16S., R.16W. Separated by an embayment is a smaller terrace, the axis of which extends from the northwest quarter of sec. 11, T.16S., R.16W., south to the southwest quarter of sec. 14, T. 16S., R.16W. The Meakin sand is productive on the first terrace, and the Nacatoch has produced a small amount of gas and oil here; on the smaller terrace, the Blossom sand is productive. One of the most prolific pools found in the Nacatoch sand in the western part of the Smackover district is located on the embayment that separates these two terraces.

#### RELATION OF OIL AND GAS TO STRUCTURE

The relation of oil and gas to the structure was studied by plotting, on the map, Fig. 1, the initial production, the thickness of sand, and thickness of productive zone in each well. An examination of this map shows the major Smackover structure to be productive of oil or gas over almost the entire area; that certain localities are much more productive than others can be attributed to the difference in the configuration of the strata of the major fold and to the relation of the porous medium to the structure.

#### *Nacatoch Sand*

The loose sand beds of the Nacatoch horizon are intercalated with indurated layers of sand and beds of gumbo and shale. These impervious sediments act as an effective barrier between the different porous layers, some of which contain oil and gas. Gas in the upper part of the horizon is found over the entire Smackover district, except in a few localities of

small extent in the western part, where no porous beds exist. The pressure and volume are greatest on top of the Norphlet dome, where the wells have an average open flow capacity of 45,000,000 cu. ft. of gas in 24 hr., and a rock pressure of 850 lb. per sq. in. The volume of gas decreased only slightly down the north dip and large oil wells were obtained almost to the edge of the productive area. Down the east and south slopes, the volume and pressure decreased gradually away from the crest of the dome and, consequently, only small oil wells were obtained near the edge of the structure in these localities. The pressure and volume on the western slope, down to the axis of the Kenova saddle, were usually large, with a maximum open flow volume of about 25,000,000 cu. ft. daily. Large quantities of oil are found on the western side of the dome.

In the Burton pool, the open flow volume of some of the gas wells ran as high as 30,000,000 cu. ft. on the relatively flat part of the structure in sec. 29 and the western half of sec. 28, T.15S., R.16W. Oil is found on the relatively steep slope in the eastern half of sec. 28 and the western half of sec. 27, T.15S., R.16W. The line of contact between the oil and gas coincide, approximately, with the line that marks the change in dip. There is a belt of Nacatoch oil, about  $\frac{1}{2}$  mile wide, which extends southward from sec. 28 into the eastern half of sec. 33, T.15S., R.16W., and connects with the Broderick and Calvert pool to the south in sec. 9, 10 and 16, T.16S., R.16W. The oil and gas in the Broderick and Calvert pool are found on the relatively steep southeast slope that borders the Louann terrace. The plane separating oil and salt water on the north and east sides of the Norphlet dome has an average depth of 1910 ft. below sea level; on the south side it is about 30 ft. higher.

### *Meakin Sand*

Oil and gas occur in the Meakin sand entirely on the Louann terrace in the northwestern part of the Smackover district. The western boundary of the Meakin production extends about  $\frac{1}{2}$  mile west of the range line between R.16-17W. The area extends about 2 miles east of this range line over the relatively flat area of the Louann terrace. Southward the production runs to the edge of the terrace but the extension to the northward has not been determined.

The plane separating salt water and oil is very definite; it is found about 2150 ft. below sea level, which coincides about with the 1790-ft. contour on the Nacatoch horizon. Dickson-Springer, Campbell No. 1, in 13, T.16S., R.17W., which is an isolated well in the extreme southwestern part of the Smackover district, is an exception to this; oil was found 2185 ft. below sea level. The elevation used to determine this correlation has not been checked. Whether there is an error in elevation

or well measurement, or whether this is a separate accumulation of oil from that farther north in the Meakin sand is not determinable.

Dry gas is found on the top of the Kenova saddle in the Meakin sand at about 2220 ft. below sea level, or about 70 ft. below the plane of the salt water and oil in the Meakin sand on the Louann terrace. The open-flow capacity of these wells runs about 30,000,000 cu. ft. daily. One well far down on the south slope of the Norphlet dome has been drilled to the Meakin sand in the eastern part of the Smackover district; no other well has yet drilled below the Nacatoch sand on the dome.

### *Blossom Sand*

Two areas of production in the Blossom sand, neither of which is of great value commercially, occur in the western part of the district. The small terrace in sec. 10 and 11, T.16S., R.16W., is productive in the Blossom sand on the south and east sides; and in the southwestern part of sec. 4 and the northwestern part of sec. 9, T.16S., R.16W., oil is found on the southeastern part of the Louann terrace. Whether production is present in the Blossom under the Norphlet dome is not known, as the higher part of the structure has not been tested.

### WATER IN THE SANDS

Water in the Smackover district can be conveniently divided into three general classes; top water, water that comes from above the first producing sand; bottom water, water that lies below the producing sand and is separated from the oil and gas by impervious beds; edge water, water that holds oil and gas on the higher structural position.

#### *Top Water*

There is a great amount of top water in the Smackover field in the various sand beds in the Tertiary system. There are, however, two water sands that are important because of their persistence and because of the great volume of water they carry. These horizons are termed locally the "500-ft." and the "900-ft." sands.

The 500-ft. sand is found at an average depth of 500 ft. below the surface and about 1400 ft. above the top of the Nacatoch. It is about 50 ft. thick and consists of unconsolidated soft white to yellow sand. The water, which is fresh, has a maximum flow of 20,000 bbl. per day. The 900-ft. sand is found at an average depth of 950 ft., and usually consists of about 90 ft. of soft sand. The water may be fresh or brackish and in several wells it has been slightly salty. The maximum water flow from this sand is about 20,000 bbl. per day.

The gas liberated from the cratered wells causes the pressure that makes these large flows, and which has led many to believe that the



water is artesian. Much trouble in drilling has been caused by these two water horizons, as at their depths the pressure exerted by a column of drilling fluid may not be great enough to hold the water down; when these water flows start, they bring to the surface large amounts of sand, causing the formation of a cavity with the consequent loss of the hole.

### *Bottom Water*

A study of the Nacatoch horizon shows it to be very difficult to determine the exact positions of the oil, gas, and water, with relation to one another, for the sands are of different porosities, and contain thin shale partings and layers of indurated sandstone. Streaks of water under pressure are found by some wells rather high up in the sand, which fact led many drillers to decide that bottom water had been struck, and it was so recorded in the logs. These streaks are thin water sands that extend into the oil sands, separating the producing beds oftentimes into two or more parts.

Where bottom water is encountered on the north, west, and south sides of the Norphlet dome at an average depth of 1925 ft., it is separated from the oil and gas by thin layers of calcareous sandstone. This water has not been found in all wells as in several localities the sand is quite variable, impervious shale and gumbo being found at the horizon in which water was expected. A stray lens of water sand lies about 25 ft. above the bottom water, and is encountered in wells in sec. 6, except in the extreme southwestern portion, and the northwestern part of sec. 5, T.16S., R.15W., and a small part of sec. 1, T.16S., R.16W. This water is separated from the oil and gas by the thin layers of cap rock and is continuous beneath with the main body of bottom water. The top of this water is found at a depth of about 1900 ft. below sea level. On the east side of the Norphlet dome, and embracing practically all of the territory east of a line from the center of sec. 15, T.16S., R.15W., north to the center of sec. 33, T.15S., R.15W., bottom water is found at a depth of 1900 to 1910 ft. Along the eastern edge of the field, this water horizon merges with the edge water.

In the western part of the Smackover district, where the accumulation of oil and gas occurs in a sand lens, little or no salt water has been found. The Burton area, up to November, 1923, had no salt water. In the Broderick and Calvert pool, a few wells record salt water below which another productive horizon is sometimes found.

### *Edge Water*

Water is found on all sides of the Norphlet dome backing up the oil and gas, with the exception of the western side. On the northern and northwestern sides, edge water was found about 1910 ft. below sea level.

On the southern side of the dome, the water line is about 30 ft. higher, being found 1880 ft. below sea level. Edge water is not present on the western side of the dome as this is structurally higher than the other sides and the impervious character of the Nacatoch horizon here preclude any possibility of containing liquids.

### *Meakin Sand*

The water conditions in the Meakin sand are much more regular than in the Nacatoch. On the Louann terrace, there is apparently no separation by impervious material between the oil and gas and salt water. The line of contact between the two lies about 2150 ft. below sea level. The water extends westward under the oil, maintaining an almost constant depth. The gas in the Meakin sand, in sec. 1, T.16S., R.16W., is associated with salt water found at a depth of 2220 ft. below sea level.

### *Blossom Sand*

Water conditions in the Blossom sand are poorly known because of the inaccuracies of well records. In sec. 4, T.16S., R.16W., on the Louann terrace, salt water is found in most of the wells accompanying the oil. Southeastward and down the dip, the amount of oil in the wells decreases with a corresponding increase in the amount of salt water. The line of contact between oil and water is about 2420 ft. below sea level, which corresponds approximately to the 1800-ft. contour on the map.

## POSSIBLE CAUSES OF FOLDING

Causes of folding in the Smackover district are not well understood, but the following hypotheses have been considered and the folding may be due to one or more of them; the uneven condensation of sediments due to the differential compression of beds of sand, shale, and limestone; lenticular form of the Nacatoch sand; superposition on an erosional feature or fault scarp; tangential compression.

### *Differential Compression of Strata*

Blackwelder argues that the folding of strata, with low dips, is due to the differential compacting of sediments of shale, sand, and limestone.<sup>11</sup> He attributes the degree of folding of the strata as being dependent on the relative thickness of the underlying beds capable of being condensed. That is, beds that were relatively hard, such as limestones or sand beds, could not be compressed vertically into as small a space as muds. Evidence that this process has been effective in the Smackover field cannot be proved, but strong suggestions of it are noted. In the central part

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<sup>11</sup> Eliot Blackwelder: Origin of the Central Kansas Oil Domes. Am. Assn. Pet. Geol. Bull. (1920) 4, 89-94.

of the Norphlet dome, the Nacatoch horizon is a relatively hard calcareous sandstone, which grades laterally toward the outer part of the structure into loose sand; around the edge of the structure the Nacatoch horizon locally consists of shale.

If the lenticular form of the Nacatoch sand is a contributory cause of the folding, it would probably affect only the Nacatoch sand as this is the first producing sand encountered. At many places around the field, the Nacatoch sand pinches out; and throughout the field, it is very irregular in thickness. In a well on the east side of the Norphlet dome, in sec. 14, T.16S., R.15W., the Nacatoch sand was missing. On the north side of the district, in sec. 20, 21, and 24, T.15S., R.16W., no sand was found. Westward, from about the R.15—16W. line, the sand thins perceptibly; and in the west part of T.15S., and T.16S., R.16W., practically no sand is found.

#### *Superposition on an Erosional Feature*

The Smackover fold may be superimposed over a topographic feature on the pre-Cretaceous peneplain, or it may be superimposed on a fault scarp, the northern side being the downthrow side, in the basement rocks.

The pre-Cretaceous peneplain upon which the Cretaceous sediments were deposited may have had slight irregularities on the surface. Such a one may have existed in the Smackover area, in the form of an escarpment with a steep northern slope and gentle southern slope over which the Cretaceous and Tertiary sediments were deposited. Subsequent settling of the deposits may have caused a reflection in the younger strata of this older hill.

#### *Tangential Compression*

Compression may have been exerted to produce the major fold either from the geosynclinal prism of sediments on the south, or from the ancient land mass on the north, known as the Ouachita mountains, or from a combination of both. There has apparently been another force acting from the east, probably the pressure exerted from the geosynclinal prism of sediments to the east. This evidently produced the north and south axis of the Norphlet dome, the corresponding northern half and southern half of the El Dorado field, and the similar axes of the Sabine and Monroe uplifts.

### CAUSES OF ACCUMULATION

#### *Nacatoch Sand*

The cause of accumulation in the Nacatoch sand is thought to be a combination of structural conditions, lenticularity, and discontinuity of reservoir beds. On the Norphlet dome, the accumulation is controlled on the north, east, and south sides by the flanks of the dome: on the west

side an effective barrier is formed by shale, gumbo, and calcareous sandstone. If the hydraulic theory of the accumulation of oil is accepted, the direction of accumulation is from the south and southeast, as the contact of water and oil is lower on the north than on the south side and on the north side of the field the Nacatoch sand generally pinches out. In the western part of the Smackover district, the accumulation is caused by the lenticularity of the sands. The sand in the Burton pool is thickest in about the center and thins to the north and south and grades into impervious sandy shale to the west and east. In the Broderick and Calvert pool, the sand lensing is very evident. In the northern part of sec. 9 and 10, T.16S., R.16W., production is derived from a lens in about the center of the Nacatoch; farther south, in the north part of sec. 16, T.16S., R.16W., oil is derived from a lens farther down in the horizon. The narrow strip of production that connects the Burton and the Broderick and Calvert pool is not entirely productive, as only in certain localities does the Nacatoch contain porous sand. The hydraulic theory can hardly account for the accumulation in the western part of the field as the discontinuity of oil would prevent the migration of fluid through the sand lenses; furthermore, little or no water is found in them. It is assumed that the oil is derived from the black shales that underlie the Nacatoch and form a part of the Marlbrook formation; and that oil has migrated vertically from the Marlbrook formations upward into the porous beds of the Nacatoch. It is assumed, in this part of Arkansas, that the black shales of the Marlbrook are probably a source of the oil that is found in the Nacatoch.

#### *Meakin Sand*

The accumulation in the Meakin sand is caused mainly by structural conditions, and by the textural changes in the sand that prevent the migration of the fluid up the dip. On the Louann terrace, the accumulation is blocked on the west by the impervious layers of sandstone filled with calcareous cement; on the south and east sides, salt water backs up the oil. It is probable that the fluid migrated from the south and that the oil may be derived from the overlying black shales of the Marlbrook formation. On the west side of the Kenova saddle, in secs. 2 and 3, T.16S., R.16W., no porous sand is found at the Meakin horizon, but farther east, in sec. 1, T.16S., R.16W., gas is found. It is thought, therefore, that the gas is affected by the textural change on the west and by the configuration of the strata on the other three sides.

#### *Blossom Sand*

The accumulation in the Blossom sand is caused by structural conditions and discontinuity of porous sand beds. The productive areas of this sand are on terraces and the accumulation up the dip is barred by the decrease in the porosity of the oil-containing beds.

## PRODUCTION

The daily production of the entire field during the month of September was 108,000 bbl. of oil from 960 wells. The largest daily production, from the smallest number of wells, was during the latter part of December when about 100,000 bbl. of oil daily was produced from about 130 wells.

### *Initial Production*

A study of the initial production of the wells was made in order to note their relationship to the structure of the field, and also from the viewpoint of the effect on the neighboring wells. The initial production map, Fig. 1, was made by plotting the first 24 hr. gage. It does not show the exact relationship of the initial productions to one another, because drilling in the northwest part of the field was practically completed before active drilling commenced elsewhere. As a result of the waste of gas in this drilling, there was a great decrease in the pressure of the gas, which decreased the initial output of wells. Attempts were made to draw a curve showing the decline of initial production because of decreased gas pressure and then refer the initial production of all the wells to the original pressure in the field, but in a field of this size conditions are quite variable, so the attempt was unsuccessful.

### *Nacatoch Sand*

The initial production of the wells producing oil from the Nacatoch was dependent on the position of the well with reference to the structure, the amount and porosity of the sand encountered, and the proximity of neighboring producing wells.

The north and west sides of the Norphlet dome and the north part of the Kenova saddle formed the first productive area. This, as a whole, was one of high oil production and wells with large initial production, 5000 to 20,000 bbl., are scattered over it. As a rule, these gushers offset wells with small initial production. The wells with the large initial production, 10,000 to 20,000 bbl., were practically all brought in during the first few months of drilling, as there was no conservation of the gas during the first 8 months, with the result that the gas pressure diminished considerably. This decrease was probably one factor that caused a decline in the size of the wells that were drilled later on the dome. On the east and south sides of this fold, the largest wells were found just below the gas and farther down the slope; near the edges, the amount of gas decreases with the result that small wells were finished near the edges. The position of the wells with reference to structure in the western part of Smackover was of minor consideration.

The amount and porosity of the sands are probably the next most important factors concerning initial production. The constituents of

the Nacatoch horizon change laterally over short distances in the amounts of sand, calcareous sandstone, shale and gumbo.

The wells with the large initial production always had a relatively large amount of porous or "loose" sand. Many wells that were most favorably located with reference to structure were either small or barren because of little or no porous sand in the oil-producing horizon.

The proximity of adjacent producing wells had an important bearing on the size of the initial production. As a rule, the first well drilled to the producing horizon in a certain locality obtained the largest flush production; the offset wells were generally much smaller, although the sand, structural conditions, and gas pressure may have been very similar. This was the primary reason for the rapid and intensive drilling program pursued in the field. Observations lead to the belief that the drainage of oil to the wells consists of channels leading from all directions into the well, and that the first well drilled establishes such channels which offset wells drilled later cannot break into.

The initial production of the wells in the Nacatoch sand was from 10,000 to 25,000 bbl. of oil daily; the average is 1050 bbl. The largest well completed in the district was the Burton Trustee, Hughes No. 1, in sec. 28, T.15S., R.16W. This well was not under control for about one week and the first gage after it was brought under control showed a production of 25,000 bbl. in 24 hours.

### *Meakin Sand*

The area of high initial production of the wells finished in the Meakin sand is on the southeastern part of the Louann terrace, where the gas pressure is much greater than on the remainder of the terrace. The largest initial production of a well in the area of high production was 4000 bbl. per day and the average initial production of all wells completed in the Meakin sand is about 165 barrels.

### *Blossom Sand*

The largest initial production of wells completed in the Blossom sand was on the small terrace in sec. 10, T.16S., R.16W., where the maximum initial production of a single well was 300 bbl. The initial production of wells on the southeast part of the Louann terrace was about 50 barrels.

## DRILLING METHODS

Rotary drilling is used in the Smackover district, though a few wells were drilled into the productive sands with cable tools. The Louisiana type wooden derrick is used; it is 112 ft. high and 24 ft. square at the base. The rotary equipment varies from old to new style rotaries, with single-cylinder steam engines.

The well is started with an 18-in. bit on the end of a 6-in. drill stem, and the hole drilled 40 to 100 ft. A 15-in. conductor casing is then set and cemented and drilling is continued with a 14½-in. bit to a depth of about 600 ft. There, if necessary, 10-in. casing can be set in order to shut off the large artesian water flows found above that depth. If the water flows are successfully mudded off, the 10-in. casing is not necessary and the size of the hole is reduced to 9½ in. Drilling is continued to a depth of about 1980 ft. with a 9½-in. bit on a 4-in. drill stem, where the 6-in. casing is set and cemented. If the lower producing formations are to be tested, in case the test on the first producing horizon found at 1950 ft. to 2150 ft. is dry, 8-in. casing is set instead of the 6-in. casing. Usually the casing is set in gumbo. The 6-in. casing is set with 75 to 100 sacks of cement, and allowed to stand for at least 6 days. The single-plug method for setting the casing is the one most widely used.

After 6 days, the casing plug is drilled and the casing seat tested; the well is then ready to drill in. This is done with a 5⅞-in. bit, on drill pipe, which is made up of 200 ft. of 3-in. on the lower part and 4-in. on the upper part; this size hole is carried through the oil sand.

After completing the hole to its total depth, the liner is set. Most wells are finished with a perforated liner but in some cases a screen liner has been used. The perforated liner consists of 4½-in. or 6-in. line pipe with drill holes. The usual practice is to set perforated pipe opposite the entire thickness of possible productive sand. This takes from 60 to 80 ft. of perforated pipe for the first productive sand and only about 20 ft. for the deeper producing horizons. Back-pressure valves are put in the bottom of the liners where drilling has stopped in soft sand, but where drilling has stopped in a hard streak no back-pressure valve is used. Enough blank liner is used above the perforated pipe to come up into the casing about 25 ft. Some operators have tried to increase the amount of oil from a well by setting blank liner opposite the gas sand and by setting perforated liner opposite only the oil-bearing sand; this has been only partly successful because the oil and gas are contained in the same sand and it is not possible in a rotary-drilled well to note the contact of the two. A wooden wash plug in the lower part of the liner, and just above the back-pressure valve, serves as a guide and packer to the wash pipe. The function of the wash pipe is to carry all the mud down through the perforated pipe, so that it may pass up outside the liner and casing. On the top of the liner is attached a packer, which is used to secure a tight joint between the top of the liner and the casing into which the liner projects. Wash pipe, which is usually 2-in. line pipe, is made up and put into the liner, the bottom of the wash pipe being held in place at the bottom of the liner by the wooden wash plug and the top of the wash pipe fits into a swedge nipple so that it may be withdrawn after the well is washed. The liner, packer, and the wash pipe are then run on a

string of drill pipe to the bottom of the hole and the well is washed with clear water. The length of time that a well should be washed is a matter of personal opinion, and varies from a few hours to a day. Some operators do not wash their wells but depend on the gas cleaning the walls of the productive sand.

After setting the liner and washing out the mud from the sand, the drill pipe used for setting the liner is rotated and the liner is released. The pipe above on the top of the liner is let down upon the packer and the lead in the packer is forced out against the casing. This insures a good tight pack. The drill stem is then removed from the hole and the casinghead fittings attached.

The casinghead fittings are known as a "Christmas tree" and consist of a cross placed above the master gate from which lead the two flow lines, each of which is provided with a gate valve. A nipple and another gate valve are placed above the cross. After the "Christmas tree" is put into place and the lead lines connected the well is ready to be bailed.

Mud and water are then bailed from the hole and emptied into the slush pit. The bailer is run until all of the mud and water has been cleaned out of the hole and the oil allowed to flow through the perforated liner and to the top of the well. In many cases, in the Smackover district, the gas pressure is so great that the hole cleans itself and the well starts to flow after the bailer has been run a few times.

The mechanical methods most commonly used for raising oil are the standard rig pump, compressed air, and swabbing. When a well that does not flow is brought in or when a well has stopped flowing it is "put on the beam" in order to pump it. This necessitates the building of a standard rig such as is universally used in "hard rock" oil fields for operating a string of standard cable tools. There are no central pumping power plants in the field, therefore every well has its own pumping installation run by a gas engine. The swab is much used in wells where the productive capacity is greater than can be handled by the standard rig pump. Compressed air is used in wells where water is mixed with the oil to such an extent that large quantities of fluid must be handled to secure the maximum output from a well. The central air-pipe system is used in this district and consists of suspending the air pipe directly inside the casing. The air passes down the central pipe, which is usually 2-in. tubing, and the fluid and air discharges between the air pipe and the well casing.

#### DECLINE AND ULTIMATE PRODUCTION OF WELLS

It is practically impossible to obtain any definite idea of the ultimate production of this field, because of the dependence on a number of factors besides geologic conditions—such as the use of compressed air, swabbing, and the handling of the well.



*Nacatoch Sand*

The total recovery of oil from the Nacatoch is going to be much less than the thickness of this horizon would indicate, because usually only a portion of the sand contains oil and gas. The north and northwest sides of the Norphlet dome will produce the greatest amount of oil because this area was the first section drilled and, therefore, it had a relatively high gas pressure. In addition, there is a greater amount of porous sand capable of containing oil in the Nacatoch horizon than elsewhere in the field. The flush wells lasted about 40 days. When the wells stopped flowing, they were either swabbed or compressed air was applied to them. The swabbing is less desirable than the air, as it has a tendency to suck in salt water; also the amount of oil produced in a day was not nearly as great as that of a well subjected to air. A well that has an initial production of above 2000 bbl. usually produced about 1500 bbl. of oil per day on swabbing, and as much as 10,000 bbl. of oil per day when subjected to air. After swabbing or the use of compressed air became unprofitable, the wells were pumped and yielded 50 to 300 bbl. daily. The wells on the east and south sides of the dome produced, as a whole, less oil and declined much more rapidly than the wells on the north and northwest sides, because the active drilling of this area did not start until about six months afterwards and the gas pressure on the Norphlet dome had decreased to about one-half of what it had been at the opening of the field. The Nacatoch horizon also contains less porous sand capable of containing oil. The average age of a flowing well is about 25 days; the average pumping output of a well here is about 100 bbl.

Decline in output of oil and gas is much more rapid in the western part of the Smackover district. The gas pressure in the Burton area was much greater than elsewhere in the western district; also the thickness of the possible oil-bearing sand is greater, as much as 50 ft. being logged, which is about 40 ft. more than the average well possessed in the west district. The flowing wells lasted about 20 days, and the pumping wells averaged about 75 bbl. In the Broderick and Calvert pool, flush production lasted only about 10 days, and the wells pumped about 60 bbl. daily. In the productive area connecting these two pools, the flush production lasted only for two or three days and the wells pumped only about 40 bbl. The decline in the wells is very rapid, as there is only about 5 ft. of producing sand in this area.

*Meakin Sand*

The decline of wells in the Meakin sand is much less than those in the Nacatoch. The wells with the large initial productions, 1000 to 4000 bbl., flowed about 30 days. The average wells have a flush production of about 175 bbl., and some of these wells flow for as long as four

months. The pumping wells average about 75 bbl. daily, and decline very slowly. This horizon is the most consistent producer in the field.

*Blossom Sand*

Very few of the wells completed in this sand flowed. The largest flowing well completed made about 300 bbl. of oil the first day; flush production lasted only two or three days. These wells make about 50 bbl. daily when put to pumping but soon decline; and after they are pumped for about a month the production is only about 20 bbl. per day.

## The Electrical Dehydration of Cut Oil

By F. D. MAHONE, LOS ANGELES, CALIF.

(Tulsa Meeting, October, 1923)

Much crude oil, as produced from the well, carries varying amounts of water, which may be present as free water in globules sufficiently large to settle out, in time, if the fluid is allowed to stand, or as an emulsion formed by myriads of minute water particles, each surrounded and entrapped by a film of oil through which it cannot break under the action of gravity alone. Such an emulsified mixture of oil and water is commonly termed "cut oil."

When such an emulsion is subjected, under proper conditions, to the influence of a high-potential alternating-current field, the minute water particles rupture the enveloping oil films and coalesce into larger water droplets this procedure continuing until all the water is freed into drops of such size that they readily settle out. This action has been photographed by the micro-moving-picture camera; under the microscope, the breaking-up of the emulsion, as described, is seen to be accomplished in a few seconds.

The low power requirements of the process, from records of commercial plants, substantiate the theory that the action is that of a multitude of electrical condensers in series, rather than that of a number of conducting paths. The minute water particles serve as the metallic elements, or plates, of the condensers and the separating oil acts as the dielectric. Such surface charges as the particles may have are removed, and the intervening oil is broken, probably electrically by the voltage and mechanically by the attractive force between adjacent oppositely electrified particles.

The principle of breaking up an emulsion under the influence of an alternating electric field was discovered by F. G. Cottrell and Buckner Speed, through experiments conducted, at the University of California, which resulted in a plant being installed on the property of the Lucile Oil Co. in the Coalinga field, California, early in 1909. This plant was able to reduce 14-per cent. emulsion to less than 2-per cent. with commercial success.

### STANDARD COTTRELL APPARATUS

The present standard Cottrell apparatus consists essentially of the electric treater and a settling or trap tank. The treater is a galvanized-iron tank approximately 3 ft. in diameter and 10 ft. high, which con-

stitutes the grounded electrode, and a number of circular disks mounted on a vertical shaft concentric with the shell and slowly revolved by gearing from a small motor. These disks form the live electrode, which carries approximately 11,000 volts and is properly insulated from the gearing and the rest of the treater. It is charged from one side of a high-potential transformer (the other side being grounded), the primary of which is excited from a commercial 220-volt alternating-current circuit through a suitable switchboard and regulating coil. Within the treater is a steam coil for controlling the temperature of the emulsion undergoing treatment. The cut oil enters the treater continuously and flows through the electric field formed at the annular space between the edges of the disks and the treater shell, where it is broken up, and the oil and water, now in the free state, pass to the trap tank. Here the water, with foreign matter and the salts held in solution, is continuously drawn off from the bottom, while the cleaned oil, taken out at the top through an adjustable swing pipe, flows continuously to the shipping tanks.

The capacity per treater, depending on the character of the emulsion and other conditions, ranges from 200 to 1000 bbl. of pipe-line oil per day. The power consumption is between 25 and 75 watt-hours per barrel of cleaned oil; the cost of electricity, at 1.5 cents per kw.-hr., averages 1 cent for 10 to 25 bbl. The total cost, including steam, electricity, royalty, labor, repairs, interest, and depreciation is from  $\frac{3}{4}$  to 3 cents per barrel of net oil. This type of dehydrator is in general use in California, having recovered, in 1922, over 15,000,000 bbl. of pipe-line oil from cut production containing from 5 to 75 per cent. emulsion and averaging between 30 and 35 per cent. The gravity ran from 11° to 35° B $\acute{e}$ . The largest plant has fifty-four units and requires two operators.

#### NATIONAL TREATER

In the Gulf Coast fields, the National treater has been found to be better suited to the local conditions than the Cottrell. No trap tank is required, as the treater, 8 ft. in diameter and 15 ft. high, provides ample settling space for the treatment of Gulf Coast emulsions. On account of the relatively large throughput, preheating, by means of heat exchangers or otherwise, is usually employed. However, the treater is provided with a welded-in steam coil for temperature regulation and use in starting up. The electric field consists of a number of flat sheet-iron plates, alternately live and grounded, which are suitably suspended vertically in the upper portion of the treater. The live plates are charged to 11,000 volts alternating current. Cut oil is introduced near the bottom, passes up through warm water into the electric field and is there resolved into clean oil and free water, the former flowing directly from the top of the treater to the shipping tanks, and the latter being bled from the bottom through a gooseneck, which insures that the treater must always be full. The

treating tank, built of riveted boiler iron, is entirely enclosed, and the system, from supply pump to shipping tanks, is completely vapor tight. The capacity of a National unit ranges from 500 to 3000 bbl. of pipe-line oil per day, the cost of treatment being about the same as with the Cottrell. In 1922, National treaters cleaned nearly as much oil as did the older type.

#### NEW HF TREATER

After considerable experimental work in field and laboratory, extending over several years, a treater has been developed from which certain undesirable features of former types are eliminated and which has several distinct advantages of its own.

The cut oil to be treated enters the electric field immediately on entering the treater. This causes the switchboard voltmeter to register early any evidence of incomplete treatment there may be, thereby minimizing the chance of sending partly cleaned oil to the shipping tanks. The direction of flow through the field is almost horizontal, so that when the water settles, it takes the shortest path out of the remainder of the fluid and out of the field. An excess of salt water in the field affords too great conductivity, which lowers the difference in potential between the electrodes, and thus retards treating action. The electrodes are in the lower half of the treater, the upper portion containing cleaned oil. This makes insulation of the live electrode a simple matter and obviates insulator and bushing troubles.

A novel method of agitation prevents prolonged short-circuiting and tends to maintain the required voltage. A float-operated contactor switch automatically opens the primary transformer circuit, should the treater oil level fall too low. It is thus impossible for a gas pocket at the top of the treater to become electrically ignited. The distance between electrodes may be quickly and easily altered, making the treater very flexible for changing conditions. Other advantages are ease of installation, portability, simplicity of operation, safety in life and fire hazard, low depreciation, and low cost, in terms of barrels per day of throughput.

The first commercial installation of this type of plant was in the Montebello field, California. One unit successfully cleaned 3000 bbl. per day. Several plants are in operation at Signal Hill, treating from 1500 to 2000 bbl. per day of cut oil. A single unit installation at Luling, Texas, reduced 1600 bbl. per day, which was the pump capacity, of 20-per cent. emulsion to less than 0.5-per cent. emulsion, working at a temperature of 82° F.

#### HEATING AND GASOLINE LOSS

In a few instances, with the electrical process, no heating is required and the cut oil enters the treater as it comes from the well. Usually,

however, some heat is supplied, principally as an economic measure to increase the capacity of the plant. The effects of heating are to lower the viscosity and to increase the difference between the specific gravity of the oil and of the water. Some extremely viscous and rebellious California emulsions must be raised to 180° F. to secure a proper cost relation between fuel consumption and throughput, while lighter oils treat satisfactorily at 120° F. or less. The average treater temperature of all California plants is 135° F. Where a relatively high treater temperature is maintained, the use of heat exchangers will save fuel by giving heat to the incoming cut oil, and will lessen the loss of volatile matter in the cleaned oil by cooling it immediately as it comes from the treating tank. In both of the newer type treaters, the system may be made vapor tight from supply pump to shipping tanks.

#### UNINTERRUPTED OPERATION

The electrical process gives best satisfaction when operated continuously, as a saving in heat, electric power and labor is effected. Unless a quantity of sand, mud or other solid matter is supplied to the treater, there is no need for cleaning the apparatus, an operation which consists only in removing a manhole cover and slushing out with a hose. All water-soluble salts pass out in the water, and nothing is added to the oil for the refinery to contend with later. Although the power is supplied in the form of electricity, the separation is purely a mechanical one. Retreatment has never been found necessary, the first run giving oil-free water and, to pipe-line requirements, water-free oil.

#### GENERAL APPLICATION

The outstanding feature of the electrical process is its lack of limitation. It is handling, though not with equal ease, all types of oil-field emulsions, of all percentages, viscosities and gravities.

#### DISCUSSION

H. F. WRIGHT.—Do any plants in the Mid-Continent fields use this method?

MR. MAHONE.—There are no plants in Oklahoma. The process has never, I believe, been tried on fresh production there. It has, however, been tried on tank bottoms, but with very poor success.

MR. WRIGHT.—What is the reason for this?

MR. MAHONE.—It is difficult to treat cut oil that has been heated, boiled, and allowed to stand and cool, unless this is mixed with fresh production. There was a six-unit Cottrell installation at El Dorado,

Kans., that operated successfully on fresh production, and, I believe, on tank bottoms, probably mixed.

MR. MILLIKEN.—What is the effect of the electrical process when the percentage of emulsification is very large, yet the percentage of water is very small?

MR. MAHONE.—That is rather unusual, is it not?

MR. MILLIKEN.—That is the principal condition that exists at Smackover.

MR. MAHONE.—Two National type plants are operating in the Smackover field. One is operating quite successfully on a mixture of fresh production with storage oil; the other is a new installation—I do not know what it has accomplished.

## Separation and Purification of Liquids by Centrifugation, with Special Reference to Petroleum

By A. F. MESTON, NEW YORK, N. Y.

(Canadian Meeting, August, 1923)

CENTRIFUGAL force has been used for centuries for separating liquids but machines for doing this are a comparatively recent development. The use of these machines is being extended into many industries but this paper is confined to their use in the oil industry. The centrifugal machine is found at the well where "cut oil" is dehydrated for acceptance by pipe lines; and in the refinery and byproduct plant. In fact, wherever finely divided suspended particles should be removed from an oil, there is a possible use for a centrifugal machine, if the particles have, or can be made to have, a specific gravity different from that of the oil. Centrifugal machines are also used for cleaning fuel and lubricating oils and dehydrating transformer oils.

### APPLICATIONS AND RESULTS

When oil comes from the well mixed with water, it is spoken of as *cut oil*. Settling often does not remove sufficient water for the oil to be accepted by pipe lines, thus necessitating chemical or other treatment. Centrifuging alone, or following chemical treatment, effectively prepares such oil for pipe lines, as is shown by the following data:

	TEMPERATURE, DEGREES F.	OIL TO PIPE LINE, BBL. PER HOUR	WATER, ETC. AT START, PER CENT.	WATER, ETC. AT FINISH, PER CENT.
Oklahoma lease....	160	10	10	0.25
Kansas lease .....	125	4	20	0.25 to 2

On the Oklahoma lease, the machine was cleaned of solid material once in 12 hr. At first, it was thought that chemical treatment was necessary to start separation and 1 qt. of prepared compound was added to each 100 bbl. of the cut oil before centrifuging. Later it was found that



if the oil settled somewhat before centrifuging, chemical treatment was unnecessary; heat and settling alone would not break the emulsion satisfactorily. On the Kansas lease, the oil was of 22° Bé. with very small gasoline content.

In Fig. 1 is shown an improvised set-up on a lease; the installations should be protected whenever possible because heat exchangers can be more conveniently used with them; heat exchangers save heat and furnish a means of quickly heating and quickly cooling the oil—an essential factor in minimizing gasoline losses, which is of great importance

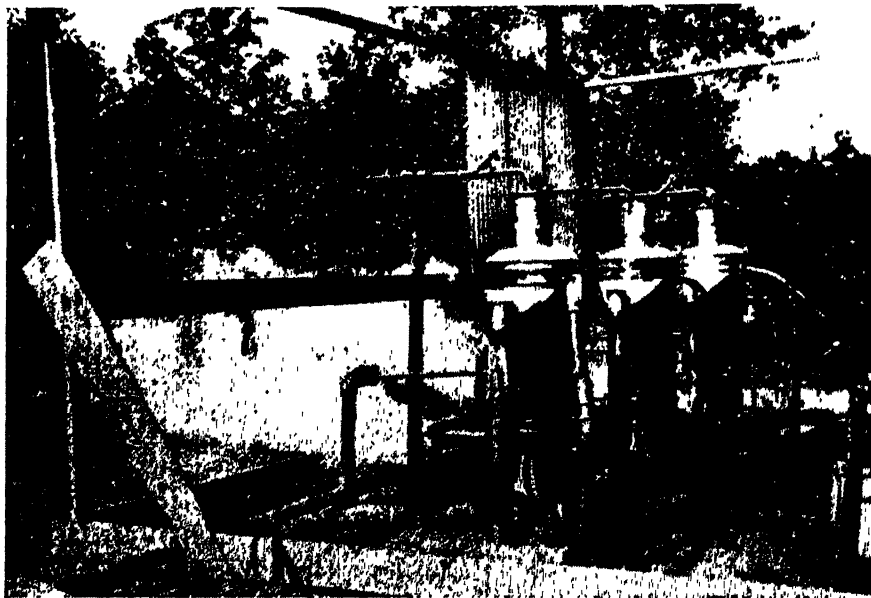


FIG. 1.—INSTALLATION ON LEASE.

when crude oil is purchased on a preferential basis. By their use, the uncleaned oil going to the machines receives much of the heat necessary for effective separation from the purified oil that is leaving the machine.

#### *Oil from Storage and Tank Bottoms*

Oil from storage tanks is cleaned in much the same way as cut oil. The oil is heated, sometimes given a preliminary chemical treatment, and passed through the centrifuge. Heavy oils are harder to run than light oils and higher temperatures are required. The amount of contamination and the extent to which they are emulsified largely determine the rate at which they can be cleaned. The following results were secured on 16° Bé. Texas coastal crude taken from storage; one of the tanks ran as low as 14° Bé., necessitating the higher tem-

perature indicated. Chemical treatment, using about one-fourth as much chemical as was used for gravity settling, was found helpful.

OIL FROM EARTHEN STORAGE, TEXAS COASTAL, 14°-16° BÉ.			
TEMPERATURE, DEGREES F.	TO CENTRIFUGAL, BBL. PER HR.	BOTTOM SETTLEDINGS PLUS WATER CONTENT INGOING, PER CENT.	OUTGOING, PER CENT.
180-200	5-8	10 (aver.)	0.25-3.0

### *Refinery Applications*

At the refinery, crude petroleum is stilled and the products are chemically treated, filtered, blended, and compounded. When refineries were supplied with high-grade Pennsylvania crude, they had no great difficulty turning out high-grade products. Today the refineries are handling



FIG. 2.—FOUR OIL PURIFIERS IN PLANT OF ASSOCIATED OIL CO.

many different crudes, so chemical and special treatments are required if the finished products are to meet the exacting specifications. Experimental work defines the processes, which are then carried along on a large scale under careful control and supervision.

Centrifugal machines are well adapted to processes requiring careful control and are used extensively in experimental work and when special products are made. Extensive tests have shown that much is to be gained by complete dehydration of some crudes previous to their stilling, as much of the magnesium salts and other detrimental substances can be so removed. One refiner finds it advisable to put all his transformer oil through centrifugal dehydrators previous to shipping. Fig. 2 shows a refinery installation.

*Manufacture of Bright Stock*

Centrifugal machines furnish the most effective means for economically producing low-pour bright stock. *Bright stock* is the product obtained by filtering cylinder stock (the still residue, with 600° F. fire test, from a paraffine-base crude) and then removing the amorphous waxes. These waxes (petrolatum) separate out and congeal, when left in the filtered oil, at comparatively high temperatures and prevent the oil from flowing or pouring. It has been the practice to remove the



FIG. 3.—INSTALLATION FOR MANUFACTURE OF BRIGHT STOCK.

petrolatum by cold (gravity) settling, but centrifugal machines are now being used because of the more complete separation that can be obtained.

Cylinder stock from Pennsylvania crude, blended with naphtha, filtered, and chilled to below 15° F. can be centrifuged at a rate of 200 to 300 gal. of blended oil per hour per machine. The bright stock in solution with naphtha flows from one spout of the machine and comprises 85 to 92 per cent. of the ingoing solution. The remainder of the solution sludges out of another spout—when a low-bowl centrifuge is used, and consists of the amorphous waxes and naphtha. When the long-bowl

type of centrifuge is used, the waxes pass out with a liquid (brine or hot water) carrier.

The oil or bright stock, after the naphtha is driven off, will have a pouring temperature of 20° to 30° F. The reduced waxes or petrolatum will have a melting point of 125° to 140° F. Fig. 3 shows a bright-stock installation.

### CENTRIFUGAL FORCE

A body in motion moves in a straight line when not influenced by other forces. When a body, or particle, is made to move in a curved path, the reaction of the body, or particle, against the force that causes it to move in this path is called *centrifugal force*. It is equal to the restraining force but opposite in direction.

If the particle moves with uniform speed about the center of rotation, the centrifugal force

$$F = \frac{MV^2}{R} \quad (1)$$

in which  $M$  = mass of moving particle;

$V$  = speed of moving particle;

$R$  = radius of circle

$$M(\text{in pounds}) = \frac{W}{32.17}$$

where  $W$  = mass, in pounds.

$$V(\text{in feet per second}) = \frac{2\pi RN}{60}$$

where  $R$  = radius, in feet;

$N$  = number of revolutions per minute.

Substituting in (1)

$$F = \frac{W}{32.17} \times \left( \frac{2\pi RN}{60} \right)^2 \div R$$

$$F = \frac{WRN^2}{2933} \quad (2)$$

The pull of the earth on a mass of 1 lb. is a force of 1 lb.; centrifugal force acting on a rotating mass of 1 lb. exerts a pull of  $\frac{RN^2}{2933}$  lb. Using this last expression, the centrifugal exerted force by any machine can be compared directly with the force of gravity.

In machines using centrifugal force to separate materials of different specific gravities, the force available to produce separation depends on the difference in specific gravity of the two materials. (The values in the formula just given were based on the weight of a body in air.) If a particle is suspended in a liquid which weighs, in air, half as much per unit volume as does the particle, the effective pull a centrifugal

machine will exert on the particle is one-half of what it would have been had it been suspended in air; if the liquid weighs three-fourths as much, the effective pull is only one-fourth as great. The effective force on a particle suspended in a liquid is, therefore,

$$F' = \frac{W\left(1 - \frac{S_1}{S_2}\right)RN^2}{2933}$$

where  $F'$  = effective force, in pounds;

$W$  = weight of particle in air, in pounds;

$S_1$  = specific gravity of liquid;

$S_2$  = specific gravity of particle.

If  $S_1$  is greater than  $S_2$ , the force is negative; that is, the particle tends to move inwardly toward its center of rotation.

### CENTRIFUGAL MACHINES

The effectiveness with which a centrifugal machine removes suspended particles from liquids depends on the magnitude of the centrifugal force it exerts, the length of time the force acts upon the particles, and the distance the particles must move through the liquid before separation is accomplished. Very small particles suspended in a liquid and acted upon by a constant force, settle at a more or less constant rate. Starting from rest, a small particle cannot obtain any appreciable velocity before the resistance set up by the liquid equals the force causing the acceleration and a constant rate of settling results; therefore, the time necessary for separation is directly proportional to the thickness of liquid to be transversed by the particles, assuming that the force acting remains constant.

Almost as important as the removal of the particles, is the prevention of their re-entering the purified liquid. Eddy currents must not exist and the incoming unprocessed liquid must not come in contact with the outgoing purified liquid; and in the passages where the separation takes place, the particles or droplets must be compelled to coalesce upon and move along one side of a passage, only, while the main body of liquid from which they are being separated keeps to the other side of the passage as it moves in the opposite direction. Fig. 4 illustrates how inclined conical disks are used to divide the mixture to be separated into thin layers and how they permit a realization of the other conditions mentioned. A centrifugal machine equipped with a bowl constructed as shown will be very effective even at moderately high speed.

The centrifugal machines used for dehydrating and purifying oils are intended for processes requiring more or less continuous operation. They will continuously sludge out most of the impurities that oils contain, but where sand and similar substances are met, some of the heavy

material is retained in the bowls of the machines and periodical cleaning is required.

One type of machine in common use rotates at 6000 rev. per min.; another at 17,000 rev. per min. Such speeds are above the critical speeds of the machines; that is, at these high speeds the revolving bowl and spindle do not revolve around their geometrical axis but around an axis that goes through their center of mass. One type of machine, which supports the bowl from below, permits this change of axis to take

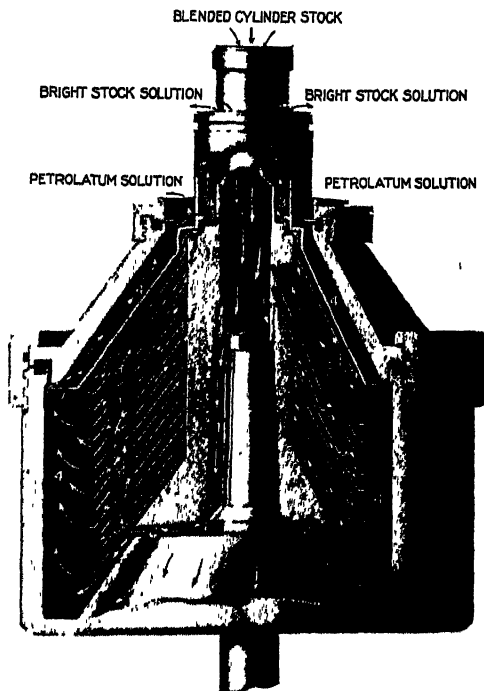


FIG. 4.—CONSTRUCTION OF BOWL WITH DISKS.

place by providing a flexible guide bushing for the spindle just under the bowl. There is no bearing or guide above the bowl. In the other type of machine the bowl is suspended and rotated by a flexible spindle.

#### SUSPENSION OF PARTICLES IN LIQUIDS

Finely divided and highly dispersed particles stay in suspension because they are of the same specific gravity as the liquid (which is not common) or because the liquid is so viscous that precipitation cannot take place, or because the particles are so small that molecular bombardment and electrical forces have a greater effect on them than does

the force of gravity.<sup>1</sup> Extremely small particles may never settle by gravity alone but most particles will settle if given time enough. Stokes<sup>2</sup> has offered the following formula, which has been quite generally accepted, for computing the rate of fall:

$$V = \frac{2r^2(S - S')g}{9n}$$

where  $V$  = constant rate of fall;  $r$  = radius of particle;  $S$  = specific gravity of particle;  $S'$  = specific gravity of liquid;  $g$  = gravitational constant;  $n$  = coefficient of viscosity of liquid.

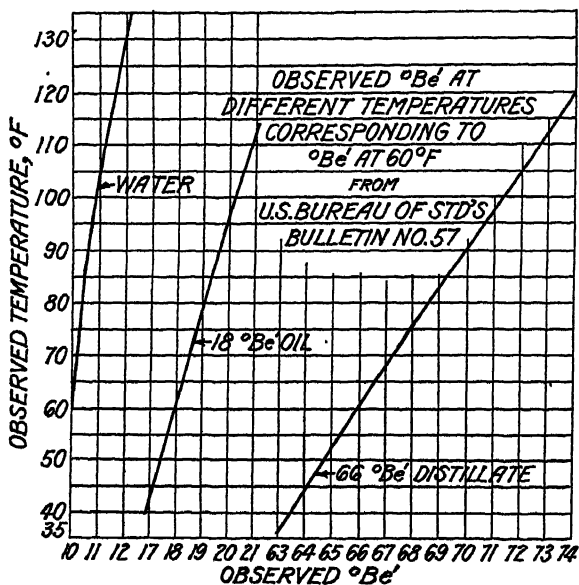


FIG. 5.

From this formula, the rate  $V$  at which the particles will fall through the liquid can be increased if  $r$  or  $(S - S')$  can be increased, or if a greater force than  $g$  can be applied. On the other hand, a decrease in the viscosity  $n$  will aid settling. The obvious way to increase the size of the suspended particles is to cause them to agglomerate or coalesce; this subject will be discussed later. The use of centrifugal machines as a means of obtaining a force greater than  $g$  has already been discussed.

A common method of increasing the difference between the specific gravity of the particles and of the liquid is to change the temperature of the mixture, especially when the particles are droplets of water or oil in water and oil emulsions. Fig. 5 shows the weight, in terms of degrees

<sup>1</sup> Jean Perrin: "Atoms," 87. N. Y., 1916. D. Van Nostrand.

<sup>2</sup> "Mathematical and Physical Papers," 3, 1901. Cambridge Univ. Press. E. Cunningham: *Proc. Roy. Soc.* (1910) 83A, 357.

Baumé, of water and the weight of typical oils at different temperatures as compared with the weight of water at 60° F.<sup>3</sup> A rise in temperature decreases the weight of a unit volume of the oil more rapidly than that of water (because its mean coefficient of thermal expansion is greater) and makes separation and settling easier to accomplish.

Chemicals are sometimes used to change the specific gravity of liquids. Common salt added to water makes a solution heavier than water and will aid in removing particles that are about the same specific gravity as water. Naphtha is added to oils to get liquids of lower specific gravity than the undiluted oils.

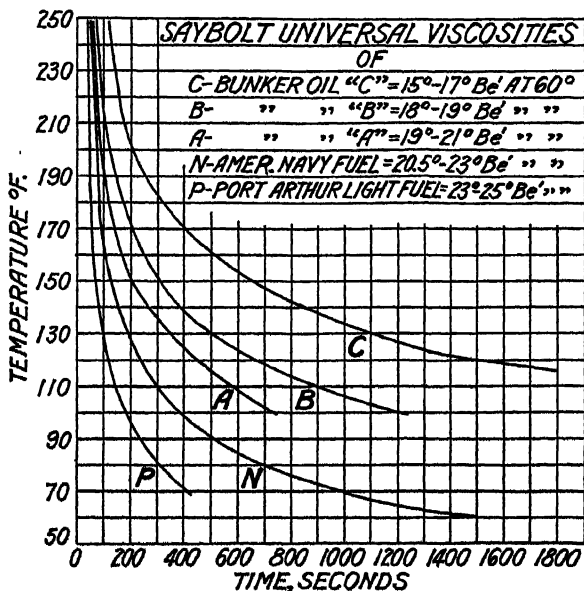


Fig. 6.

To decrease  $\eta$ , that is to make the liquid less viscous, the liquid can be heated. Fig. 6 shows the variation of viscosity with temperature in the case of a number of oils. A solvent may be added to decrease the viscosity; naphtha is added to oils, turpentine to paints, and alcohol to gums.

### SOLS, GELS, AND EMULSIONS

A sol is a suspension of extremely finely divided particles in a liquid.<sup>4</sup> The particles may be so small that the molecules of the liquid, darting

<sup>3</sup> U. S. Bur. of Stand. Cir. 57; Tech. Paper 77.

<sup>4</sup> Edward W. Washburn: "Principles of Physical Chemistry," 436. N. Y., 1921. McGraw-Hill Book Co.



back and forth because of their kinetic energy, keep the particles moving and they do not settle. The movements of these small particles (they are thought to be  $1\mu$ , which is 0.000001 meter, or less, in diameter<sup>8</sup>) caused by the molecular bombardment are called "Brownian movements."<sup>8</sup> Particles less than  $0.5\mu$  are kept moving so vigorously that they never settle by gravity, so they must be agglomerated before they can be removed by gravity settling or, if extremely small, by centrifugation. The agglomeration is called a gel.<sup>7</sup>

Small particles in suspension do not coalesce and agglomerate because each one has absorbed on, or in, its surface either an electric charge or some protective film.<sup>8, 9</sup> (Perhaps the explanation should be in terms of electric charges in either case.) Particles so protected are said to be peptized. Before precipitation can be realized, the protective film must be neutralized or removed; this is commonly done by adding chemicals—electrolytes.<sup>10</sup> Heating too near the boiling point of the liquid may do it; a strong electric field, as in the Cottrell-Wright-Speed process,<sup>11</sup> effectively breaks down the films in some emulsions.

Agglomeration may be brought about by filtering the liquid. In refinery practice, there is an interesting illustration of peptizing substances preventing particles from agglomerating; and the removal of these substances by filtering through fuller's earth results in the subsequent formation of a gel. The residual obtained by running down paraffine-base crude in a fire and steam still until it gives a 600° F. fire test, contains the amorphous waxes known as petrolatum. It also contains impurities, seemingly black in color, which are called asphalt or tar bodies. This heavy lubricating oil left in the still with the petrolatum and the impurities in it, will flow, or pour, until it is cooled down to 50° or 40° F.; but after the impurities are filtered out, the waxy particles that make up the petrolatum agglomerate so readily that they prevent the oil from pouring below 85°, sometimes 100° F., and necessitate the removal of the petrolatum before the oil can be used as bright stock. Of course, the tar bodies may have something to do with the solubility of the waxes. It is not claimed, however, that the phenomena are totally explained in this simple fashion.

<sup>8</sup> W. Oswald and M. H. Fischer: "Theoretical and Applied Colloid Chemistry," 162. N. Y., 1922. John Wiley & Sons.

<sup>9</sup> Jean Perrin, *loc. cit.*

<sup>7</sup> Wilder D. Bancroft: "Applied Colloid Chemistry," 162. N. Y., 1921. McGraw-Hill Book Co.

<sup>8</sup> Ridsdale Ellis: *Zeit. Phys. Chem.* (1912) 80, 597.

<sup>9</sup> Graham: *Jnl. Chem. Soc.* (1864) 17. S. E. Sheppard: *Jnl. Ind. and Eng. Chem.* (1921) 13, 37.

<sup>10</sup> Burton: *Phil. Mag.* (1906) 12; (1909) 17.

<sup>11</sup> U. S. Patents, 987114, -5, -6, -7.

The term gel<sup>12</sup> is broadly applied to all precipitated sols or colloids. It is applied to flocculent and crystalline precipitates as well as gelatinous agglomerates.

An emulsion is a mixture of immiscible, or but slightly miscible, liquids.<sup>13</sup> One of the liquids is continuous and is known as the external or dispersing phase; the other (or others) is suspended in the first liquid in very fine droplets, and is known as the internal or dispersed phase. Usually water is the dispersed phase in a water-and-oil emulsion but sometimes it is the continuous phase and the oil is in droplets. The fine droplets of an emulsion are prevented from coalescing by protecting films,<sup>14</sup> similar to the films on the particles of a sol. The film-forming substance that gets into the interface between the water and oil is called an interfacial, or emulsifying agent. Soaps, tars, finely divided solids, and probably electric charges,<sup>15</sup> merely, act as emulsifying agents. An emulsion in which finely divided sand or silt reinforces the film made up of some other emulsifying agent is especially difficult to break.<sup>16</sup>

Some chemists and technologists attack an emulsion through the theory that films charged with unbalanced electric charges are surrounding the particles,<sup>17</sup> and if the chemical used will liberate ions of opposite sign in, or at, the interface, neutralization will take place, the droplets will coalesce, and separation of the liquids be made easy. They call attention to the greater effectiveness of bivalent and trivalent substances over monovalent ones. Ferric chloride,  $\text{FeCl}_3$ , and aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , are quite active in this respect with many emulsions, while sodium chloride,  $\text{NaCl}$ , is relatively weak. On the other hand, many technologists use chemicals to dissolve something in the liquid of the dispersed phase (or in the interface) that will lower the surface tension of that liquid and so promote coalescence. For example, oleic-acid mixtures are sometimes used to break water-in-oil emulsions.<sup>18</sup> Oil-soluble substances, like rosin soap,<sup>19</sup> can be used to break oil-in-water emulsions; the difficulty is to get the soap out of the oil afterwards.

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<sup>12</sup> Wilder D. Bancroft: "Gelatinous Precipitates and Jellies," 236. N. Y., 1921. McGraw-Hill Book Co.

<sup>13</sup> W. Clayton: Soc. Chem. Ind. London (1919) 38, No. 10.

<sup>14</sup> S. M. Pickering: *Jnl. Chem. Soc.* (1912) 91, 2002.

<sup>15</sup> H. Helmholtz: *Wied. Ann.* (1879) 7, 337. Dr. The. Svedberg: *Papers Faraday Soc.* (1920).

<sup>16</sup> S. M. Pickering: *Jnl. Chem. Soc.* (1907) 91, 2010; T. R. Briggs: *Jnl. Ind. and Eng. Chem.* (1921) 13, 1008.

<sup>17</sup> Wilder D. Bancroft: *Jnl. Phys. Chem.* (1915) 19, 363; J. L. Sherriek: *Jnl. Ind. and Eng. Chem.* (1920) 12, 133.

<sup>18</sup> U. S. Patents 1223659.

<sup>19</sup> G. H. A. Clowes: *Jnl. Phys. Chem.* (1916) 20, 417.

The work of Hatschek,<sup>20</sup> Langmuir,<sup>21</sup> and others has done much to give a clearer conception of the principles underlying surface tension, and so encourage the solution of emulsion problems with less of the hit-or-miss methods that formerly prevailed; for instance, the blowing up of oils in refinery agitators. Sometimes agitating tends to break an emulsion; sometimes it makes the emulsion "tighter."

Gibbs<sup>22</sup> discovered that a substance dissolved in a liquid will concentrate in the surface layer if by so doing it will decrease the tension or energy of the surface layer relative to the body of the liquid; but if it is a substance that raises the surface tension of the liquid, it will remain in greater concentration in the body of the liquid than in the surface. In other words, a liquid (gases and solids, too) always tries to decrease its surface energy and distributes substances within itself with this end in view. Soaps and other substances found in emulsions, which lower the surface tension of one or other of the phases, will, therefore, tend to concentrate in surface films. In "blowing up" an emulsion in an agitator or tank, a great amount of surface is created in the forming of the bubbles. Some of the soaps and other substances will concentrate in the bubble films and be carried off as a froth; some will stay behind. In this redistribution of the contaminating substances, there is the possibility of getting the proper balance of surface tensions and having the emulsion break; there is also the possibility of carrying away needed solvents and securing a tighter emulsion.

## DISCUSSION

THE CHAIRMAN, MR. WRIGHT.—Is this method of separating wax from stocks to take the place of the wax press now used?

A. F. MESTON.—No; centrifugal machines are used almost entirely for the removal of the waxes that are in such finely divided form that they are said to be amorphous. These are commonly removed by cold (gravity) settling. These waxes have high boiling points. They are solidified and agglomerated by refrigeration and, associated with considerable oil, make up the product that the practical refiner calls "petrolatum," "pet," or "petrola." The term "wax" has been limited in the past to the crystalline wax pressed from the light neutrals and re-run distillates. By leaving larger and larger fractions in the still as residuals and handling these as the cylinder stocks are now handled—in centrifugal machines—a greater portion of lubricating oils will receive centrifugal settling, and less will be left for the wax press.

<sup>20</sup> "Physics and Chemistry of Colloids," 1919. Phil. P. Blakiston's Son & Co.

<sup>21</sup> "Mechanism of the Surface Phenomena of Flotation." *Proc. Faraday Soc.* (1920) 15, Pt. 3, 62.

<sup>22</sup> J. W. Gibbs: Scientific Papers 1 and 2. See works of Roozeboom.

## Centrifugal Removal of Wax from Petroleum Lubricating Oils

BY LEO D. JONES, PHILADELPHIA, PA.

(Tulsa Meeting, October, 1923)

THE use of the centrifuge for dewaxing lubricating oils grew out of the effort to secure better results than had been attained by the common "cold settling" process. This process was the only known method for dewaxing steam refined cylinder stock (600° F. fire test), the product known as "bright stock" being commonly used for building up "pressed," i.e., dewaxed neutrals of, say, 200-sec. viscosity to a higher value. The process consisted of mixing the cylinder stock with approximately one and one-half times its volume of naphtha, heating to dissolve completely all the oil and wax and then slowly chilling to about 15° F. in large insulated tanks. This caused the wax to precipitate. It was allowed to settle out by gravity. The supernatant liquid was then drawn off and the naphtha distilled off, leaving a still residue of bright stock. The sediment from the settling, of a slushy nature, was withdrawn. After removing the naphtha by distillation the residue was petrolatum. At some point in the process, preferably after the dilution but before chilling, the mixture was decolorized by percolation through fuller's earth.

The finished bright stock produced by this process had a cold test of about 50° F. Efforts to improve this by chilling to a lower temperature resulted in a considerable reduction in yield, and increased uncertainty of settling. Even when chilling to 15° F. it was not uncommon to find that after a week's waiting a tank had not settled. It was then necessary to heat and recool. This uncertainty was a serious problem; in one case a refinery superintendent had men riveters hold pneumatic hammers against the tank for hours, hoping thus to cause agglomeration and settling of the wax. Yields of bright stock above 70 per cent. were uncommon.

### HISTORY OF CENTRIFUGAL APPLICATION

It is not surprising, therefore, that many attempts were made to improve upon the results obtained by cold settling. George H. Taber, vice-president of the Gulf Refining Co., Pittsburgh, Pa., made a number

of experiments with cream separators in 1890 but had done nothing more. The only centrifugals available were of the cream separator type. Such separators are not suitable for the separation of two liquids. They serve only to concentrate a dispersed phase of an emulsion into a fraction of the continuous phase, and it is hardly to be expected that they would have handled a liquid and a plastic solid.

It was shortly after putting into general use centrifugal separators employing the principle of hydrostatic balance that P. T. Sharples took up the investigation. He discovered that the wax, as separated by centrifugal force, differed from the slushy liquid separated by gravity. It was a plastic of too high a "yield" value to act freely as a liquid under the forces within the centrifugal rotor. It was only with considerable difficulty and by using a rotor of the hydrostatic balance type that adjustments could be made to give a discharge of wax and that only for short periods. It was necessary to upset slightly the hydrostatic balance to offset the resistance of the wax to flow, and then a condition of unstable equilibrium was obtained. This was because the resistance of the wax and also its density were not constant, but varied with the time it was exposed to centrifugal force. If, for instance, there was a slight reduction in capacity, this permitted the wax to remain in the rotor longer, with the result that it became more dense and offered more resistance to flow, both of which caused the wax layer to become thicker. Thus the action became cumulative, resulting in overcrowding the rotor with wax.

While the above uncertainty of operation can be minimized by using a centrifugal of much lower centrifugal force, the softer wax obtained and the lower yield of oil make it undesirable.

### SOLID DISCHARGE

All of this trouble was soon overcome by the invention of the so-called "solid discharge." A stratum of a third liquid substance, heavier than either of the two separated substances, was maintained within the rotor. This served two purposes. One of these was the provision of a frictionless surface on which the wax might float and flow. The second and more important was the provision of a uniform and non-resistant liquid with which to form a hydrostatic balance with the wax-free oil layer in the bowl. The rotor was then adjusted, as if the wax were not there, so as to give a maximum thickness of oil layer without allowing any oil to discharge with the carrier liquid. Any separated wax formed a thin layer between the oil and carrier liquid and soon leaked out with the latter. The operation became entirely independent of the condition of the wax and a stable equilibrium was obtained instead of an unstable one.

Calcium-chloride brine refrigerated to the same temperature as the chilled oil was used as a carrier liquid, and fed in such small quantities as to make its presence evident in the wax discharge.

This development of the solid discharge centrifugal rotor with the use of a carrier liquid marked the beginning of the commercial use of the centrifuge in the production of bright stock.

### TOP FEED

Since this original development an improvement of practical importance has been made in the method of maintaining the stratum of carrier liquid. Formerly it was fed to the rotor with the chilled oil, flowed through the rotor at a very low rate and discharged over the inner edge of a ring on the rotor. The discharge was kept at a minimum. The writer has replaced the feed in contact with the chilled oil by a jet of carrier liquid directed within the above mentioned ring. This is known as the "top feed." When the rotor is empty the carrier liquid flows into it downward instead of upward, but once the rotor has been filled to the edge of the ring any further addition pours out over the edge of the ring. This avoids any necessity for refrigeration of the carrier liquid, in consequence of which the economic prohibition upon supplying heat to the wax cover is eliminated, so that the wax may be melted upon its discharge and readily conducted from the centrifuge, also it avoids admixture of the carrier liquid with the chilled oil. This arrangement has eliminated the tendency to produce sometimes a slight cloud in the finished oil and to interfere to a certain extent with wax separation. A higher yield of oil and a better cold test are thus obtained.

### CHILLING

The effectiveness of the centrifuge in removing the wax from the chilled oil is entirely dependent on the manner in which the diluted oil is chilled. We have found that the most satisfactory method is as follows: A tank provided with brine circulating coils is used as a container for the oil mixture. The coils extend from top to bottom of the tank and are either grouped at the center of the tank or extend around the wall, leaving the center clear. Either arrangement produces a natural convection current down around the coils and upward through the remaining space.

The oil mixture is heated to about 100° F. until all wax is in solution and all moisture settled out. The mixture must become bright, otherwise a faulty precipitation of wax is likely to occur. The mixture is then transferred to the chilling tank. Brine is circulated through the coils at a temperature not more than 10° F. lower than the oil.

This differential is carefully controlled so as to give a chilling rate to the oil of about 3° F. per hour. Such control is easily accomplished as follows: A circulating pump is put in series with the coil in the tank, continuously recirculating the same brine through the coil. A regulated quantity of cold brine from the brine cooler is admitted to the suction of the pump and an equal quantity of warm brine withdrawn where the coil leaves the tank. Every hour the oil in the tank is turned over by a slow moving agitator. This insures an equal distribution of temperature and precipitated wax.

Chilling is continued until the desired temperature for centrifuging is reached. Chilling by the above method to -10° F. and centrifuging at that temperature will produce a bright stock from most crudes of 15° F. cold test.

Chilling at a slower rate than that given above has shown no advantage in cold test and is more expensive in equipment. More rapid chilling causes an increase in cold test, the increase becoming more rapid as the time of chilling is reduced. A rate greater than 5° F. gives poorer results than chilling more slowly and centrifuging at a higher temperature.

If instead of maintaining a small differential between the brine and oil, slow chilling is accomplished by allowing a small quantity of brine to enter the chilling coil, a portion of the oil is exposed at once to a low temperature, resulting in what we have termed "shock" chilling. As a result the wax is precipitated throughout the oil in a colloidal state, and cannot be separated by gravity or centrifugal force.

It is important, therefore, in order to insure an economical use of refrigeration and an effective use of the centrifuge, first to dissolve the wax completely and then slowly and uniformly chill the mixture to the required temperature for centrifuging.

### DILUTION

Three conditions must be fulfilled in the dilution of the cylinder stock: First, the viscosity must be sufficiently reduced to permit crystal formation rather than colloidal precipitation, and to permit the removal of the wax after it has precipitated. Second, the density of the mixture must be reduced below that of the wax. Third, sufficient volume of liquid must be provided for free suspension of the precipitated wax.

The first two conditions are easily accomplished by using one and one-half volumes of naphtha of about 60° Bé. With some cylinder stock, however, such as those from Wyoming crudes, the wax content is so high that the wax particles begin to crowd each other, joining together before precipitation is complete. Satisfactory separation is then difficult. In some such cases the use of slightly more naphtha than usual

is sufficient; in others, better results can be obtained by precipitating half the wax, removing it by centrifuging, and then completing the precipitation by further chilling and recentrifuging.

#### REMOVAL OF PROTECTIVE COLLOIDS

The presence of asphaltic material and coloring matter in an oil will lower its cold test. A black cylinder stock, which has a cold test of 40° F., after acid treatment and filtration will have a cold test of 85° F. These same substances interfere with the precipitation of the wax in the production of bright stock. If a black cylinder stock be put through the dewaxing process, its cold test may be reduced to 10° F., but on treating to a light color, it will rise to 35° F. It is common practice, therefore, in order to carry on the dewaxing most effectively, to refine the cylinder stock to the required color before dewaxing.

#### YIELD

With the cold settling process, it was common to secure a yield of only 70 per cent. of bright stock with a cold test of 50° F. The centrifugal separation of the precipitated wax gives a yield of 85 per cent. of 15° F. cold test bright stock, because of the greater freedom of wax from oil.

#### OTHER OILS

Extensive investigations have been carried out to determine the possibility of using the centrifugal process for the general removal of wax from all lubricating stocks. The results have shown that the process is readily applicable to any stocks containing the wax in an amorphous form, but that additional considerations are involved in the removal of wholly crystalline wax. It has been found especially applicable to what we have designated as "long residuum," that is, a steam-refined still residue, similar to cylinder stock but amounting to about 30 per cent. of the crude—all of its lubricant—instead of 15 per cent.

The long residuum is treated, as is cylinder stock, for wax removal. A yield of 84 per cent. of dewaxed oil and 16 per cent. of wax are obtained. The finally dewaxed oil contains all of the lubricating content of the crude, without any having been broken down by a cracking distillation as is necessary when neutrals are dewaxed by pressing. The dewaxed residuum may then be split up by distillation into neutrals and bright stock. It is possible by this method of refining to obtain 10 per cent. of 200-sec. viscosity neutrals and 15 per cent. of bright stock from a Pennsylvania crude, when formerly not over 5 per cent. of 200-sec. viscosity neutral was obtained. The cold test of the neutral will be below 25° F. and that of the bright stock below 15° F.



## Centrifuging Petroleum-refinery Emulsions

BY EUGENE E. AYRES, JR., PHILADELPHIA, PA.

(Tulsa Meeting, October, 1923)

THE centrifuge has come into general use in the oil fields and in the establishments where lubricating and fuel oils are used. Probably centrifugal machinery will be found more useful in the refinery when the operators are more familiar with the principles of modern centrifugation and when centrifugal engineers better understand the refinery emulsion problems.

It is not generally realized that centrifugal force and gravity have two distinct functions: First, subsidence wherein the suspended globules are brought into contact; second, coalescence (when this is possible) by rupturing the films around the globules. In the case of a water-in-oil emulsion, an exercise of the former function alone would yield: (1) oil, free, or as free as desired, from water; and (2) a concentrated water-in-oil emulsion—concentrated in the sense that it contains a relatively large percentage of the internal phase. An exercise of both functions will yield: (1) water-free oil and (2) oil-free water.

Centrifugal force is much better than gravity for subsidence because, in the case of industrial emulsions where the suspended globules are visible under a microscope, subsidence is directly proportional to the force applied.

Centrifugal force is only slightly better than gravity for coalescence. A minute trace of a proper reagent will immediately do more to nullify the interfacial surface tension opposing coalescence than an indefinite application of the highest attainable centrifugal force. No mathematical analysis has been made to explain the failure of high centrifugal force to induce a decidedly more rapid and more complete coalescence than is obtained by gravity.

The adjustment of the centrifuge rotor depends more on the extent of coalescence that is desired or is possible than on any other factor. One reason for this dependence is to be found in the curious relation between the specific gravity and the hydrostatic pressure of emulsions. The continuous centrifuge works on the U-tube or Florentine flask prin-

ciple, and for homogeneous liquids the ratio of liquid depths is assumed to be inversely equal to the ratio of specific gravities. But in the case of emulsions where the globules have a diameter of one micron or larger, the balanced depths are not inversely proportional to mean specific gravities. For example, suppose we centrifuge an oil-in-water emulsion whose continuous water phase has a specific gravity of 1.00, while the oil is 0.80. If the emulsion is of such a character as to permit a coalescence of oil globules, we may expect 0.8 in. of the water phase to balance 1 in. of oil. If the oil globules cannot be made to coalesce, we may so operate as to form a concentrated oil-in-water emulsion containing 70 per cent of oil. The mean specific gravity of this emulsion should be 0.86, and it would be natural to expect 0.86 in. of water to balance 1 in. of emulsion. Experience has shown that this is not the case; we are likely to require 0.96 in. of water to balance 1 in. of this emulsion.

Adjustment of the centrifugal rotor depends on the type of the emulsion. In the case of water-in-oil emulsions, water is assumed to be heavier than oil. Subsidence by centrifugal force will, therefore, move the water globule outward. If the globules coalesce when they come into contact, a continuous water layer will be formed at the periphery. The coalesced water layer is equivalent to "dead" space in the sense that this water layer requires no more work from centrifugal force and yet takes up room in the rotor, thus reducing the capacity of the rotor for the oil phase. On the contrary, the suspended oil globules of an oil-in-water emulsion are presumed to be lighter than the water and will therefore be moved inward by centrifugal force. If the oil globules coalesce, an oil layer is formed at the surface; in this case it is the oil layer that is dead space. If coalescence is not obtained and the suspended globules are merely brought into close contact, the concentrated globules form a viscous, or gelatinous, layer that may also be regarded as dead space.

There are cases in which a partial coalescence may be obtained by centrifugal force. Such cases are frequent with water-in-oil emulsions and rotors are specially designed for this condition. No rotor has yet been designed to take advantage of a tendency to partial coalescence in oil-in-water emulsions because there has been no demand for such an operation. Where a partial coalescence is to be obtained (for water-in-oil emulsions) a high percentage of internal phase will require an adjustment different from that required by a low percentage of internal phase if the maximum of coalescence is to be obtained in each case.

In this connection we must take into account the viscosity of the oil and the interfacial surface tension of the emulsion. If the surface tension is low, the globules will coalesce when they are brought into contact by subsidence. If the viscosity is high, subsidence will be slow. With a low surface tension (a weak emulsifying agent) and high viscosity,

the largest possible volume of oil must be maintained in the rotor; conversely, if the viscosity is low (and subsidence is rapid) while the surface tension is high (and coalescence is difficult) it is not necessary to maintain so high a volume of oil in the rotor, but the rotor must be adjusted to maintain a relatively large volume of intermediate emulsion on which centrifugal force can work to accomplish coalescence.

The adjustment of the rotor must be governed by the quality of results desired by centrifugal resolution. In most industrial applications, results are not perfect. It is usually possible to obtain perfect results from a purely technologic standpoint; but to achieve this perfection it may be necessary to sacrifice economy. In one case of the resolution of a water-in-oil emulsion, four adjustments gave the following results, with corresponding maximum capacities:

WATER	OIL	CAPACITY, BARRELS PER HOUR
1. Free from oil	1 per cent. moisture	1.0
2. Free from oil	Free from water	1.5
3. 1 per cent. of oil	Free from water	3.0
4. 1 per cent. of oil	1 per cent. moisture	15.0

Adjustments 1 and 2 show that a change of adjustment may produce a better result at a higher maximum capacity. If the results from adjustment 4 are industrially satisfactory, that adjustment must be selected because of the economic advantage.

Suppose we have an oil-in-water emulsion from which we desire to recover the maximum yield of oil. If subsidence and coalescence are both difficult, the rotor must be adjusted to hold a maximum volume of water and a minimum volume of concentrated emulsion. In other words, in making adjustments coalescence must be sacrificed for yield and a discharged concentrated emulsion obtained instead of free oil. The importance of correct rotor adjustment will be realized when we state that the change of one of the rotor dimensions  $\frac{1}{8}$  in. may convert a prohibitively expensive operation into an attractively profitable one.

## B. S. ACCUMULATIONS

When "cut production" is dehydrated in the field by centrifuging or by chemical methods, the crude is not made perfectly dry but is merely reduced to 1 or 2 per cent. moisture. When this oil is stored for a time at the refineries, the emulsion gradually accumulates in the storage tanks. The accumulation is particularly certain to occur if reagents have been used in the field, because the reagent has counteracted the emulsifying element of the crude.

The method of resolution depends on the percentage of inorganic matter. If the inorganic matter is low, say not over 2 per cent., it is possible to centrifuge direct. In the absence of wax it is desirable to centrifuge at as high a temperature as feasible to reduce viscosity; when wax is present, a high temperature is necessary to melt the wax. If reagents have been used in the production field, an addition of reagent to the refinery accumulation before centrifuging will be without value. Otherwise the use of reagents may be of value in the case of high-viscosity crudes.

When the inorganic percentage is high, it is advisable to free the emulsion from the bulk of the solids before attempting centrifugal separation. To accomplish this the emulsion may be agitated with a solution of caustic soda, soda ash, or sodium silicate, then heated and settled. A portion of the solids may be taken up by the aqueous layer and another portion will collect between the settled layers of oil and water. Supernatant oil, after such treatment, contains a lower percentage of solids and water and can be efficiently freed of both by centrifuging.

Any water-soluble colloid will tend to break the water-in-oil emulsions. Examples of water-soluble colloids that have been used for this purpose are common soap, rosin soap, the so-called soap from petroleum, starch, glue, albumen, casein, and the gums. The soaps of the heavy metals will stabilize water-in-oil emulsions instead of tending to resolve them. The most efficient reagent that we have used for resolving water-in-oil emulsions is sodium-rosin soap containing not less than 60 per cent. dry matter. This substance is soluble in oil and can be used to advantage. Aqueous solutions of rosin soap are no more efficacious than aqueous solutions of common soap or petroleum soap, but such aqueous solutions are frequently used and are often helpful. Aqueous solutions of starch, glue, etc. will be as efficacious as the soap solutions, especially if a trace of alkali (such as caustic soda or soda ash) is added to the solution of colloid. The theory underlying the use of such substances is that the water-soluble colloids tend to produce emulsions of oil-in-water, and if a trace of such substances is used with an emulsion of water-in-oil, the tendency will be to neutralize the stabilizing effect of the hydrophobe colloid present in the water-in-oil emulsion.

#### CRUDE OIL CONTAINING SALT WATER

When crudes are distilled continuously, it is of particular advantage to remove the salt water as far as possible in order that the salt may not deposit in the still. There has been some question as to whether the salt in the crude petroleum is all in solution in the emulsified water, or whether some salt is not suspended in the oil in colloidal form. We believe this confusion has arisen from the inaccuracy of the method for the determination of salt by igniting the oil in a crucible.

Careful tests on a number of samples of crude have indicated that the salt content of the crude was directly proportional to the moisture content. The tests were made by removing by centrifugal force various proportions of the moisture content and then determining the moisture and salt in the oil. The salt was determined by a method suggested by Ralph R. Matthews wherein the oil is extracted with acetone and water and the extract is titrated. In most cases where, in cut production, the oil is partly dehydrated by heating, any salt precipitated from aqueous solution is in a relatively coarse granular form in which it readily settles out of the oil.

It can be safely assumed that to reduce the salt content of a crude we need merely to reduce the moisture. A crude oil cannot be completely dehydrated by centrifuging except at high cost. Some of the low-viscosity crudes containing under 2 per cent. water can be reduced to 0.1 per cent. moisture by simple centrifuging at high capacities.

The more viscous crudes, containing under 2 per cent. water, can be reduced to 0.1 per cent. moisture by dissolving in the oil 0.1 or 0.2 per cent. of sodium-rosin soap containing 60 per cent. or more dry matter. The oil is then centrifuged at high capacities. Oils containing more than 2 per cent. water can be reduced to 0.1 per cent. moisture, but the cost is higher. High temperatures for centrifuging are advantageous. Crudes of very high viscosity cannot be economically dehydrated with rosin soap and centrifuging.

Other hydrophile colloids may be substituted for sodium-rosin soap, but the latter has the advantage of being soluble in oil and by diffusing through the oil it comes in contact with the dispersed water globules. After centrifuging, the oil contains rosin soap only in proportion to the moisture remaining in the oil, for the bulk of the soap is in the separated water.

#### ACID SLUDGE IN OIL

If a lubricating distillate and the necessary proportion of sulfuric acid are flowed independently through a type of centrifugal machine adapted to emulsify thoroughly the acid with the oil, and within the same second to separate the emulsified material and to discharge a sour oil on the one hand and an acid sludge on the other, it will be found that the discharged oil will be practically clear and free from traces of suspended sludge. Furthermore, the discharged oil will be found to have received an acid treat as efficient as the ordinary acid treat in which acid is in contact with oil for a considerable period. But the discharged sour oil, although practically clear at the moment of discharge, will show more and more turbidity until a considerable volume of acid sludge is formed by coalescence and settles out.

This appears to be a case where the viscosity of the oil retards coalescence. In such cases we have not yet seen any reason for treating by centrifugal emulsification and separation. Oils of very low viscosity, such as the kerosene distillates, can be treated in the manner just described with a discharge of a sour oil that will not deposit sludge on standing. In the absence of high viscosity, the coalescence of sludge appears to be complete and immediate.

It may develop that the method of centrifugal emulsification and separation may have some distinct advantages over the usual methods of treating the lighter oils, but the subject has not been exhaustively investigated.

It appears to us that the centrifuge is of greatest value for the separation in some special cases of well coalesced sludge from highly viscous oils. When cylinder stock is treated in the usual fashion and the period of contact of acid and oil is sufficiently great to insure the complete coalescence of sludge, the centrifuge will efficiently separate the suspended sludge from the oil, yielding a sour oil with less acidity than could be obtained by long gravity settling. In general, when acid treats are made in the usual manner and the sludge is permitted to settle out, the supernatant oil may be centrifuged with a considerable reduction in acidity. This is merely because of the removal of traces of suspended sludge that had not settled by gravity. But it has not been found possible to remove all traces of mineral acid from even the low-viscosity sour oils by direct centrifuging.

#### EMULSIONS OF SOUR OILS AND WATER

In some cases it is an advantage to be able to emulsify a sour oil with water in order that the acidity of the sour oil may be reduced by washing. It is generally supposed that contact of water with a sour oil tends to hydrolyze the contained acid sludge with a tendency to the reversion of color compounds to the oil. Apparently this effect can be minimized, although whether or not the effect can be entirely avoided has not yet been proved. In some cases, however, slight color changes are not regarded as important. For example, when a reduced Mid-Continent crude is acid treated, it is said to be a distinct advantage to eliminate the acidity from the sour oil by some method that will avoid the formation of ash-producing substances. The difficulty with the water wash for Mid-Continent crudes is that a stable emulsion tends to form—an emulsion that will not settle out unless reagents are used. The reagents known to refineries are usually ash forming so that the water wash in this way does not accomplish ash elimination. Other reagents are decomposed by the acidity of the oil and the products of decomposition are harmful.

The emulsions formed when water is agitated with sour oils are of the type of water-in-oil and, therefore, require a hydrophile colloid for their resolution. These emulsions are frequently too stable for simple centrifugal separation. They may be resolved by agitating the emulsion with a dilute starch solution and then centrifuging, but the technique is difficult.

We have found it possible to wash a sour oil efficiently without the formation of a stable emulsion by agitating the sour oil with a starch solution. The emulsion thus formed can be completely resolved by centrifugal force. The oils treated in this fashion are clear and dry. When the oils are violently shaken in a 4-oz. bottle with water to which methyl orange has been added no change in color is observable in the aqueous layer, thus indicating the absence of water-extractable acid. However, when oils are tested according to the standard method for acidity, using a 60-per cent. alcohol aqueous layer with phenolphthalein as an indicator, and titrating with tenth-normal caustic soda, the acidity value of the washed oils amounts to about  $\frac{1}{2}$  c.c. normal alkali per 100 c.c. of oil. All of the Mid-Continent treated oils seem to give about this result, which would seem to indicate organic water-insoluble acid. The washing with starch water removes acidity from sour oils apparently to the same extent as contact with finely divided fuller's earth.

If it were considered satisfactory to distill a reduced Mid-Continent crude after such treatment, ash in the still would be completely avoided. If it is considered necessary to complete the neutralization with caustic soda, the neutralization may be made very simply without the formation of a water-in-oil emulsion. A sour oil after a starch wash can be neutralized with a caustic-soda solution of any strength with a quick and complete gravity settling. The caustic-soda solution after settling out is clear instead of being milky. Whether, under these conditions, the soaps formed by the interaction of caustic soda with organic acid are retained in the oil or are completely extracted in the aqueous layer has not been ascertained.

For the starch wash about 0.1 per cent. by weight of starch has been found to be sufficient. The temperature at which the starch emulsion must be centrifuged depends on the viscosity of the oil treated. With ordinary reduced Mid-Continent crude averaging about 105 Saybolt viscosity at 100° F., a temperature of 200° F. is used to obtain the highest centrifuge capacities and the most economical operation, but operation is practical at somewhat lower temperatures.

The best results have been obtained by emulsifying starch water with the sour oil at normal temperatures, and then warming the oils, centrifuging as soon as the oil has reached the desired temperature. In this way the effect of temperature on the color of the slightly acid oil is minimized because of the brief time during which the oil is hot. The

application of the starch wash to the preparation of finished lubricating distillates has received little attention, but there would seem to be some interesting possibilities.

### EMULSIONS OF SOUR OIL AND CAUSTIC SODA

When sour oils are neutralized with caustic soda, the products of the reaction are soap and sodium sulfate, also some free alkali. The emulsions formed are of the type of water-in-oil. The type might be explained by adsorption of the basic radicals of the inorganic salts and alkali present.

The soap would tend strongly to stabilize an oil-in-water emulsion. We conclude that the salt concentration in the aqueous phase is high enough to precipitate the sulfonic soap either in such form as to render it colloiddally inactive, or else in the form of a hydrophobe colloid. That the sulfonic soap in such emulsions is distributed in the continuous oil phase is indicated by the fact that mere contact of additional water with these emulsions will cause the emulsion to break down. The water appears to extract the sulfonic soap from the oil. It is standard practice to percolate water through alkaline emulsions or to agitate the emulsion with successive charges of fresh water.

Acid-treated oils from which all traces of excess sulfuric acid have been removed by efficient water washing or by filtration through fuller's earth can be agitated with caustic-soda solutions to remove dissolved organic acids without the formation of stable emulsions. This may be explained by the fact that no sodium sulfate is present to precipitate the sulfonic soap. The absence of sodium sulfate probably accounts, also, for the fact that the separated aqueous phase contains no emulsified oil. The petroleum soaps are probably too soluble in water to function as hydrophile emulsifying agents except in the presence of sufficient electrolyte to give them colloidal character.

It is natural that solutions of starch or other hydrophile colloids should not aid the separation of alkaline emulsions. What is necessary for the resolution of an alkaline emulsion is the presence of sufficient water to extract the petroleum soap from the continuous oil phase. There seems to be some advantage in some cases in carrying out the resolution as follows: From 20 to 60 per cent. of water is added to the alkaline emulsion and the liquids are brought into contact by agitation with live steam or mechanical agitators. The hot mixture is then centrifuged at comparatively high capacities. The discharge from the centrifuge will be clear dry oil on the one hand, and reasonably oil-free water on the other. It is possible by this procedure to secure an immediate resolution of the emulsion, which has the effect of improving color and speeding production in the case of viscous oils difficult to wash.



If sour oils have been water-washed before neutralization, immediate resolution may be obtained without the use of centrifugals. The simplicity of the caustic-soda neutralization with the entire elimination of any alkaline emulsion trouble would appear to be a strong argument in favor of water washing of sour oils, provided the water washing can be accomplished in a given case without detriment to color.

## Evaporation Loss of Petroleum—Theories and Their Application

By J. H. WIGGINS, BARTLESVILLE, OKLA.

(Tulsa Meeting, October, 1923)

GRANTING that about 600,000,000 bbl. of light oil will be produced in the United States this year and taking the Bureau of Mines' statement that  $7\frac{1}{2}$  per cent. of the total crude production will be lost before the finished gasoline is shipped from the refinery, the volumetric evaporation will be 45,000,000 bbl. of the cream of the gasoline. This is a conservative figure and is equivalent to 1,890,000,000 gal. The real value of this liquid is at least 150 per cent. of the value of an equal volume of motor fuel. At only 10 c. per gal., the value lost is \$189,000,000; at 15 c. per gal. the loss is \$283,000,000.

If 750,000,000 bbl. of light and heavy oil are produced here this year and the average price per barrel is \$1.333, the gross return to producers will be \$1,000,000,000 and the net returns about \$200,000,000, if the cost of production is only \$1 per barrel. Thus, the evaporation bill is about 20 per cent. of the gross income and is equal to the net income of the crude-oil producers.

Two other comparisons with popular phases of the petroleum industry will help give an adequate conception of the evaporation problem. These are: cost of preventing evaporation compared to cost of cracked gasoline and volume of gasoline evaporated compared to volume of gasoline manufactured from natural gas.

When gasoline is manufactured from heavy oils by the cracking process, there are two important divisions of the total cost of the product: the manufacturing cost, such as plant cost, operation, maintenance, etc., and the cost of the barrel of heavy oil, from which the cracked gasoline is made. In preventing evaporation loss the cost first mentioned enters into the total cost, but the second cost is eliminated; that is, no charge is necessary for stock from which to manufacture the saving. A detailed analysis of these two costs on a large scale shows that the net income from a dollar spent in preventing evaporation loss from the lease through the refinery is twice the net income from a dollar spent in cracking. Of

course, it is possible for cracking to become unprofitable by running up the cost of stock and running down the price of gasoline, but saving evaporation will never thus become ruinous. The lower the price of crude oil, the greater is the necessity for stopping the evaporation leaks.

Detailed figures are not available, but the natural gasoline manufactured this year may be approximately 600,000,000 gal. The evaporation loss of 1,890,000,000 gal. then is three times the volume produced by extraction from natural gas.

When such figures are quoted, it is, at first, impossible to realize why a condition so destructive of natural wealth should exist. One of the smallest causes is storage; 300,000,000 bbl. of crude are in storage today. If this storage were contained in 55,000-barrel tanks, each containing 50,000 bbl., the total oil surface would be about 1500 acres, the seams along plates that are air-leaky is about 5500 miles, and the semiconfined vapor space above the oil is about 300,000,000 cu. ft. It is unlikely that an actual survey of storage would show such efficiency of storage to surface, etc., as this.

Another and more important cause of evaporation loss is the constant filling and emptying of tanks. When a tank of oil is emptied, fresh air takes the place of the oil and is saturated with vapor. This vapor is lost when the tank is refilled. The magnitude of this loss is easily shown. The 600,000,000 bbl. of light oil is handled at least seven times before it gets through the refinery. This represents 23,583,000,000 cu. ft. of air vapor mixture that will be forced from tanks in 1923.

Many other still worse conditions could be described but these give an idea of why evaporation is one of the most important economic problems of the oil industry today.

### THEORIES INVOLVED IN EVAPORATION LOSS

In practice, evaporation can occur only by fresh air, or permanent gas, being in contact with the oil surface and by boiling. Of these, only the first applies to motor fuel (gasoline) or crude oil; boiling requires a higher temperature than is encountered for ordinary motor fuel or crude oil.

Fresh air in contact with a surface of oil acts much like a sponge and becomes saturated with gasoline vapor until the partial pressure of the vapor is equal to the vapor pressure of the liquid. As far as ultimate evaporation of the oil is concerned, 100 cu. ft. of fresh air over the oil surface is like 100 cu. ft. of perfect vacuum. The perfect vacuum would be filled with 100 cu. ft. of vapor and the total pressure in that space would then be the vapor pressure of the oil. Little has been published on vapor pressure of petroleum and its products but there are several interesting points in connection with vapor pressure that will bear discussion.

### *Blending*

One of these is the effect of mixing, or blending, a high vapor pressure hydrocarbon liquid with one having a low vapor pressure. Suppose that a gallon of 42° Bé. kerosene and a gallon of 80° Bé. gasoline are mixed. Their vapor pressures are assumed at  $\frac{1}{2}$  in. and 15 in. of mercury, respectively, when they are separate. The popular idea is that when they are mixed, the vapor pressure of the mixture remains close to that of the gasoline. As a matter of fact, however, the vapor pressure of the mixture will be reduced to 6 to 8 in. of mercury. This means that the lower hydrocarbons have an affinity or a holding effect on the higher hydrocarbons.

### *Partial Content of Vapors*

It is believed that air in contact with oil takes up, practically, only the vapor of the lighter hydrocarbons in the mixture and that, on saturation, the partial pressure of these lighter vapors keeps the more volatile hydrocarbons in the liquid phase. It is also quite probable that the presence of the vapor of the lighter hydrocarbon over a mixture of hydrocarbon liquids keeps the heavier fractions from even exerting their quota of the total vapor pressure of the mixture. Expressed in a more concrete way: If there is a mixture of pure hydrocarbon liquids of 84°, 80°, 76°, and 72° Bé. it is thought that under evaporation into the air the first vapor to come off would be nearly all 84° Bé. with a little of the 80° Bé. and practically none of the 76° and 72° Bé. If these hydrocarbons, separated, had vapor pressures of 18, 16, 14 and 12 in. of mercury, respectively, theoretically the vapor coming from the mixture should contain 12 parts of the 72° Bé. liquid in 60 parts of vapor, or 20 per cent. Tests have indicated, though, that the vapor coming from the mixture will contain considerably less than the 20 per cent. of vapor from the 72° Bé. liquid; but this point has not been definitely proved.

### *Double Nature of Vapor Pressure*

When studying the vapor pressure of petroleum, the first observation is that there are two sources of pressure: One is the true vapor pressure of the liquid, the other is the pressure set up by the expulsion of a part of the permanent gas held by the oil. As far as the breathing of a tight tank is concerned, the sum of these pressures is the effective one; therefore, vapor pressure curves that show the true vapor pressure of the liquid only may be misleading if used in the calculation of evaporation loss.

### *Permanent Gas Contained in Oil*

The question arises as to how much and in what manner permanent hydrocarbon gases are held in crude oil. Crude oil will dissolve from 22

to 33 per cent. of its volume of air. Such a solution does not involve an increase of volume of the crude, because air is not a hydrocarbon gas. However, the question is open as to how much methane or ethane, for instance, a given crude can contain and the manner in which it is held; namely, how much is held in solution as a purely permanent gas and how much may be held in a condensed liquid phase, because of what might be called an "affinity pressure" that the heavier hydrocarbons exert on the lighter ones. How the high permanent gas content affects evaporation is not known; it is known, however, that the rate is increased. How much the decrease in volume of such an evaporating crude is due to elimination of liquid permanent gas or liquid permanent gasoline is unknown.

#### *Change of Temperature and Wind and Barometric Pressures*

The expansion and contraction of a mixture of air and vapor when heated and cooled is one reason for bringing fresh air in contact with the oil surface in a gas-tight tank. To raise the temperature of the gas in a tank 30° F. means an expulsion of about  $\frac{30}{530}$ , or about 6 per cent., of the volume of gas contained in the tank. When the gas space is cooled at night, a similar amount of fresh air must be taken into the tank. This action goes on every day.

A more important source of breathing in a gas-tight tank is the alternate heating and cooling of the surface of the oil in the tank. The variation of temperature of the body of the oil has no marked effect. If the oil surface at night is 85° F., but rises to 105° or 110° F. during the hottest part of the day, the vapor pressure of the oil surface rises. As the vapor pressure rises, the partial pressure of the vapor rises. This necessitates the expulsion of an added quantity of air and gasoline vapor. On cooling at night, the vapor pressure of the surface decreases, condensation takes place, and fresh air is drawn in the tank to replace the condensed vapor. This effect, in the case of gasoline, may amount to 12 per cent. or more of the total air-vapor volume above the gasoline. It is seen that the effect of change in vapor pressure of the liquid surface is much more important than simple thermal expansion.

The fluctuation of wind velocity may have some effect on the pressure inside the tank which, in turn, might cause some excess breathing during the inactive periods of thermal effects on the gas and the oil surface. The change in barometric pressure causes a movement of air into or out of the tank; this is a very small amount, however, and is practically negligible.

The total breath of a gas-tight tank is a summation of the results of thermal expansion of the air vapor and the change in vapor pressure of the oil surface. The effect of windage should be added to this. The barometric change may be omitted because it may or may not be compensating and in any case has a very small effect.

## APPLICATION OF THEORIES FOR HANDLING OIL AND GAS ON LEASE

*Separation of Gas and Oil*

The permanent gas accompanying the oil from the well is a carrier of gasoline vapor. If this gas is in intimate contact with the oil at 30-lb. absolute pressure, it can take up only half as much gasoline vapor per pound of permanent gas as if the absolute pressure during such contact were 15 lb. This is accounted for by the expansion of the gas to twice its former size under the 15-lb. condition, meaning that twice as much gasoline vapor is required to fill that space. The conclusion is, that gas should be separated from the oil under as high pressure as is practical before the oil is run into the settling tank and also separated quickly so that at the separating pressure the gas can become as little saturated as possible.

For this purpose, where the gas is taken to a natural gasoline recovery plant, the gas and oil should be run into a large separating tank held at atmospheric pressure. As much as 3 to 5 per cent. of the crude can be evaporated by the gas in this way in the summer.

*Gas-tight Stock Tanks on Lease*

The gas-tight tank on the lease has two phases of evaporation loss. The main loss is during filling, when the saturated air is forced out through the vents. The loss of much less importance is that occurring while the tank is standing full of oil for a day or more.

A full 15-ft. diameter stock tank contains not over 100 cu. ft. of air vapor. The worse case of breathing, if this tank vents at atmospheric pressure, is on a summer's day. Under those conditions, the tank might breathe as much as 50 cu. ft., of which, as a high estimate, 25 cu. ft. is gasoline vapor. This amounts to 0.8 gal. per day. On the average for the year round only 0.3 gal. per day should be lost from this cause. This shows the folly of carrying more pressure on a lease stock tank than is necessary to give assurance of its constant gas-tightness.

When filling a 500-bbl. stock tank, about 2310 cu. ft. of air and vapor are forced out of the tank; this is 46 times the amount of air and vapor lost in 24 hr. from a similar tank while standing full. Reduced to gasoline, this amounts to about 37 gal. for one filling of the tank. It is readily understood that a pressure of several pounds per square inch held on the tank would not decrease this filling loss. The idea seems to be quite general that if a pressure of 5 to 10 lb. per sq. in. is held on a tank, the loss while filling should be less for every cubic foot of air-vapor mixture (at the pressure inside the tank) that is forced out. This is not true, however, because the crude oil exerts its actual vapor pressure inside the tank irrespective of the pressure of the air in the tank.

Connecting the lease stock tank, then, with a natural gasoline recovery plant affords considerable saving during the filling of the tank but very little while the tank is standing full. If a stock tank so connected is held under a very slight vacuum and air leaks into the tank constantly, the gasoline plant may show considerable gain in production. But this makes the stock tank a still, as every cubic foot of air that enters the tank picks up its quota of gasoline vapor before proceeding to the recovery plant. Such false and expensive profits have been found by the writer.

### *Protection against Heat*

Various kinds of protection against the sun's rays for lease tanks, such as water-top tanks and board housings or shades, have for their field of possible saving the 0.8 gal. per day for standing and the 37 gal. filling loss on the worst days of the year. They may save one-half of the standing and one-third of the filling loss. A producer must do some close figuring to determine how long such protective measures require to pay for themselves.

### *Pipe Line and Refinery Losses*

The same laws of physics apply through the pipe lines and refineries. However, the mechanical and economic problems are vastly changed by the difference in size of tank and concentration and handling of enormous quantities of stock in single places. These problems have been discussed in other publications and are only mentioned here.

## DISCUSSION

MR. WRIGHT.—When discussing this question, a lease foreman said that he had installed two 500-bbl. tanks on the lease and was using gas for the gasoline plant. He said that he had recovered 2 or 3 gal. per 1000 ft. without reducing the volume of oil in the tanks or the gravity of the oil.

MR. WIGGINS.—He does reduce the gravity. I know of cases where they claimed to have an increase in gravity, but later it was found that a mistake had been made when making the gravity tests.

MR. WRIGHT.—Would there not be a larger evaporation loss through breathing on a larger tank than on a smaller one?

MR. WIGGINS.—I have done considerable work on that proposition but do not remember the results exactly.

MR. ROUSE.—What benefit is derived by holding great pressure and what will be the difference saved on the lease tanks?

MR. WIGGINS.—In a 500-bbl. tank on a summer day (taking the worst case) there will be about 75 cu. ft. of vapor over the oil under the roof. As the outside temperature increases the gas expands and must either

breathe out or increase the pressure. It may increase the pressure 5 lb. or it may breathe one-third of the 75 cu. ft.

MR. ROUSH.—Considering the hazards that we have, I do not believe we gain anything by air-tight devices. A  $\frac{1}{4}$ -in. hole on a 250-bbl. tank, regulated according to the volume of oil running into the tank just enough to keep it at atmospheric pressure, will prevent the collapsing of the tanks.

MR. WIGGINS.—If you have a lease tank that is gas-tight and you test it periodically, you will not have much trouble from collapsing. The only thing is that the valve must hold a slight pressure in order to test the tank.

MR. ROUSH.—That could be checked up very easily by the pumpers, but they are not interested enough to see that it is done. We had four 250-bbl. tanks collapse with gas-tight valves. I believe we saved 6 in. in 7 days. We had two tanks alongside of each other, but I do not see that we gained much more than we did with the ordinary  $\frac{1}{4}$ -in. hole.

MR. WIGGINS.—Did you have one with a  $\frac{1}{4}$ -in. hole at the same time?

MR. ROUSH.—Not at the same time that we tried the tank devices. The tanks collapsed when taking out the oil. The air-tight devices have small wire screens, which become corroded and cause vacuum to form, which will pull in the top of the tank.

MR. BEHNKE.—If you have casinghead gas and connect the casinghead with the lead line so that the casinghead will flow with the lead line is there a chance of enriching the oil?

MR. WIGGINS.—You will probably enrich the gas but not the oil.

MR. BEHNKE.—How are we going to get the gasoline out of the oil? If it is entirely a matter of temperature, would it be better to bury the pipe lines?

MR. WIGGINS.—You would help to hold the gravity of the oil if you did that, but is it paying?

MR. ROUSH.—At \$4.50 a barrel it may pay to do that. The pressure on the lead line is an extra strain on the shackle rods but if you are lifting 1500 ft. already that does not matter. If on a flowing well, you will increase the back pressure.

MR. BEHNKE.—In Tonkawa field, this summer, we made some tests on gravity from 42° to 46° oil at the lease. On comparing a sample at the well and one at the end of the 500 or 600 ft. flow line, a difference of  $1\frac{1}{2}$ ° gravity was found.

MR. WIGGINS.—The exact nature of the conditions of sampling would be necessary to give an intelligent comparison with other tests,



Tonkawa crude might very easily lose 2 to 5 per cent. during the filling of a tank.

MR. WRIGHT.—The question has been raised about the value of gas tank devices from a standpoint of fire hazards. We are all interested in stopping the fire hazards.

MR. WIGGINS.—In stopping evaporation loss, you automatically decrease the fire hazards. If there is no oxygen in the tank you will not have any fire. If you have a proper mixture of air and vapor, you may have an explosion. In winter, when the vapor pressure is low, you can get a burning mixture that will blow off the roof and catch fire.

MR. ROUSH.—If you pipe that vapor straight up in the air the hazard from fire will be small. On one occasion, a tank was on fire quite a little time before it was discovered but the men went on top of the tank and put it out with wet blankets and quilts. Most of the devices are not more than 1 ft. from the deck of the tank, so that a fire will burn out the gaskets and, in a short time, will get into the tank. If the pipe is run up 5 to 6 ft. over the top of the tank that hazard can be eliminated.

If you pipe to the bottom of the tank you will save quite a bit of the gravity. Do not allow the oil to splash. Put the connection as close to the bottom as possible. The pipe-line companies may object and you may have to make some connections with open tees, so as to allow the oil to get into the tank as easily as possible. We have to steam out our lines every so often as the paraffin gathers and plugs the lines, lead lines and all.

MR. BEENKE.—How much would the gravity be lowered if it contained 1 per cent. of B. S. against a pure oil?

MR. WIGGINS.—I have not been able to do much work along that line. You will have to work pretty close, but 1 per cent. will show up in the gravity.

## Evaluation of Casinghead Gas

BY OLIVER U. BRADLEY, MUSKOGEE, OKLA.

(Canadian Meeting, August, 1923)

THE conditions affecting the supply of casinghead gas, the different degrees of productivity, the difficulty of determining the quantities utilized, and the evaluation of the gas in casinghead-gasoline units and related data, having an economic bearing on the industry as a whole, are important questions and offer an interesting field for study.

Casinghead-gas data have been gathered in some of the oil fields of Oklahoma where testing work has been done regularly and the volumes of casinghead gas were available. The area covered embraces 219 scattered leases in 29 townships, with a total of 18,039 acres and 1921 wells. The accompanying table gives specific locations of the areas under consideration, number of leases, range depth of wells, average age of production, sand depths and oil production data. The results of this investigation are set forth in the accompanying charts, showing volumes of casinghead gas in 6-month periods from Jan. 1, 1918, to June 30, 1921, when full record was available, production of casinghead gasoline, average productivity of the gas in gallons per thousand cubic feet, average price of the gas and the market price of the casinghead gasoline. The cases enumerated in the table and the data shown in the graphs do not represent the greater part of oil or casinghead gas production from any one township, nor are the leases contiguous. The properties in each township, however, may be considered as typical of general conditions, such as the date of completion of wells, depth, character, and thickness of oil sand, time of pumping, present oil production, vacuum carried on wells, and usual operating practices.

It was deemed advisable to subdivide the time into 6-mo. periods, as it was impracticable to make the tests more frequently, furthermore 6 mo. is probably the minimum period within which there would occur a noticeable increase in the productivity of the gas. It must be remembered that the figures on volumes are subject to the usual irregularities and relative inaccuracies of meter measurements of gas under varying degrees

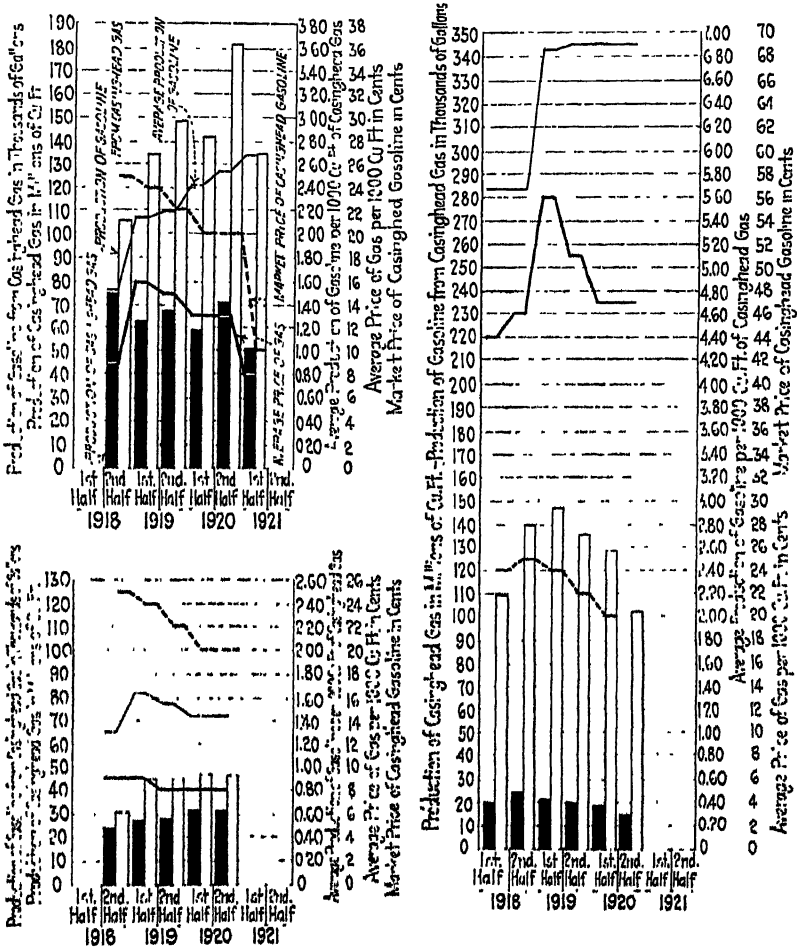
of vacuum, although all the volumes have been corrected to a normal pressure of 4 oz. When meters got out of order, the average daily volume that passed through them for the previous 30-day period was used when figuring the volumes for any one month. While this is not absolutely accurate, it is the most practical way to arrive at the amounts of gas utilized and all operators, both sellers and users of casinghead gas, accept such estimates as fair and reasonable.

DATA ON SOME OIL PRODUCING AREAS IN OKLAHOMA

Case Number	Township	Number of Leases	Total Acreage	Number of Wells	Average Age of Production, Years	Depth of Wells, Feet	Thickness of Sand Feet	Production per Acre to Dec. 1921, Inc., Barrels	Number of Acres per Well	Gravity of Oil, Degrees Baumé
1	27N, 13E	19	1,191.33	126	12.5	1,240-1,330	20-55	1,796	9.4	34-36
2	27N, 14E	5	400.00	21	9.5	1,195-1,225	15-25	621	19.0	34-36
3	27N, 15E	10	577.80	104	10.6	1,020-1,080	20-46	2,780	5.5	34-36
4	27N, 16E	8	470.00	57	13.0	640-695	15-30	2,511	8.2	33-35
5	27N, 17E	2	99.41	26	10.0	640-680	25-30	2,046	4.2	31-33
6	26N, 12E	2	152.13	17	14.5	1,350-1,390	26-60	3,303	8.9	33-36
7	26N, 13E	17	1,280.62	180	12.5	1,275-1,340	17-59	1,452	9.8	34-36
8	26N, 14E	8	739.93	83	11.3	1,040-1,115	24	1,533	8.9	34-36
9	26N, 16E	7	220.37	33	9.4	510-645	20-35	1,335	0.6	32-34
10	25N, 12E	3	163.56	7	8.4	1,370-1,465	60-85	544	23.3	32-33
11	25N, 14E	5	209.64	39	9.0	985-1,010	18-27	2,073	5.3	32-34
12	25N, 16E	8	380.00	84	13.5	500-540	18-30	1,324	4.5	31-33
13	25N, 17E	7	430.00	106	14.6	390-470	20-30	1,649	4	31-33
14	24N, 12E	4	246.68	8	11.6	1,520-1,630	70-90	593	30.8	34-37
15	24N, 17E	18	1,030.00	217	13.4	400-445	25-32	1,108	4.7	31-33
16	19N, 11E	2	200.00	6	6.5	1,875-1,980	18-30	330	33.3	35
17	18N, 7E	9	1,120.00	72	7.0	2,450-2,675	40-110	4,606	15.5	39.5-41
18	17N, 7E	32	3,520.00	332	7.0	2,450-2,700	30-120	10,990	10.6	39.5-41
19	16N, 7E	2	323.70	27	6.25	2,695-2,750	20-70	5,027	11.9	38-41
20	17N, 12E	7	826.11	82	15.0	1,450-1,575	55-80	8,862	10.0	33-35
21	18N, 12E	15	1,640.00	156	12.0	1,460-1,570	50-75	3,364	10.0	33-35
22	18N, 11E	6	600.00	43	10.0	1,450-1,500	35-65	2,017	13.9	34-36
23	17N, 14E	6	560.00	23	5.0	1,510-1,620	15-30	288	24.3	34-36
24	17N, 15E	3	240.00	17	3.75	1,140-1,190	10-25	1,413	14.1	34-36
25	16N, 11E	4	400.00	25	6.7	1,815-1,920	25-40	1,087	16.0	34-36
26	16N, 12E	2	180.00	14	7.5	1,450-1,500	30-35	1,273	11.4	34-36
27	16N, 15E	3	320.00	32	5.5	1,150-1,280	27	3,000	10.0	35-36
28	15N, 14E	3	360.00	28	6.9	1,690-1,780	18-25	1,244	13.2	33-35
29	14N, 12E	2	197.72	4	5.25	2,125-2,180	25-40	121	49.4	33-34

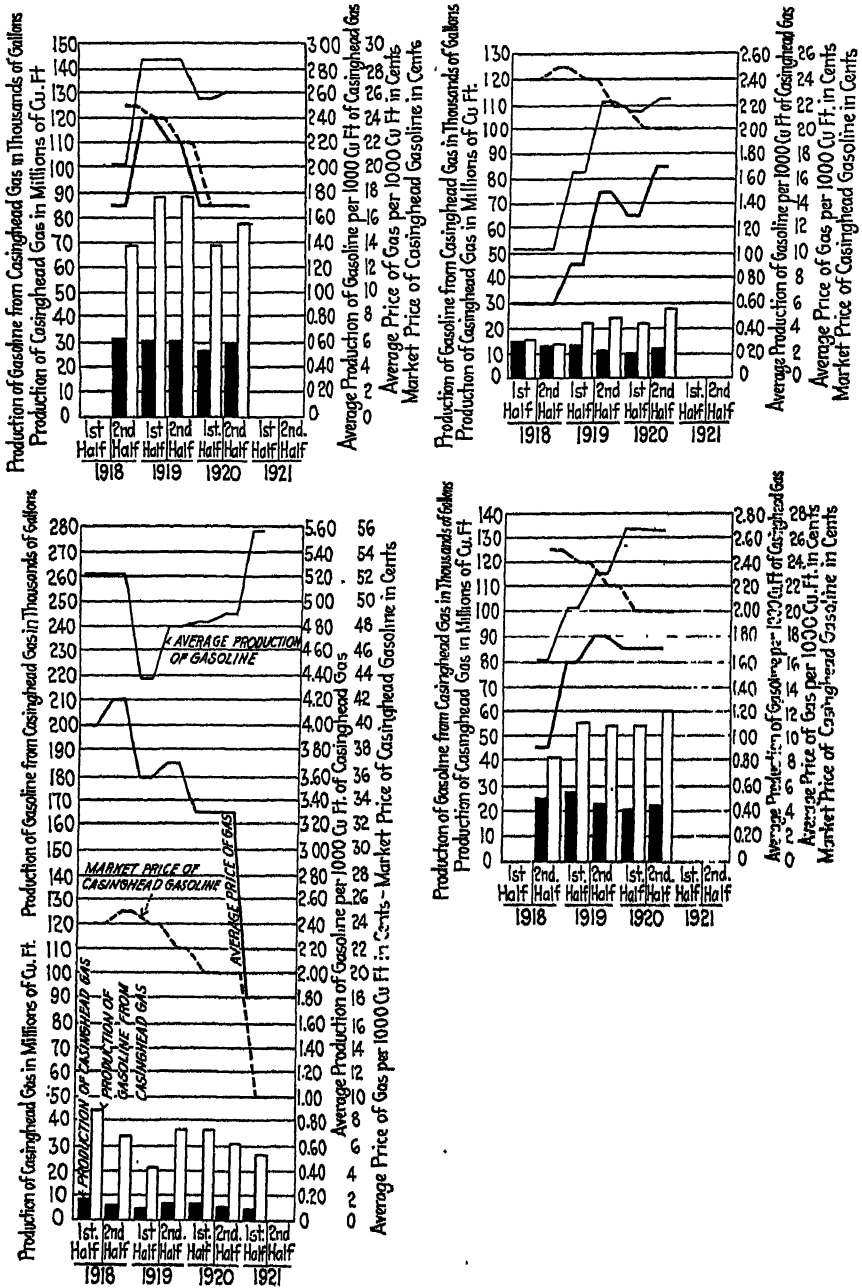
It will be observed that the figures, in many instances, fail to show any rapid or alarming decrease in casinghead-gas volumes over the 6-mo. intervals specified, or, in fact, through the entire period of 3½ years. No doubt there is a relationship between the exhaustion of the oil content of the sand and the supply of casinghead gas derived therefrom, but the nature of this relationship has not been studied. The probable progres-

sive increase in points of vacuum carried on the wells and the efficiency of its application must also be considered when noting the relatively small percentage of depletion of the gas supply in some cases.

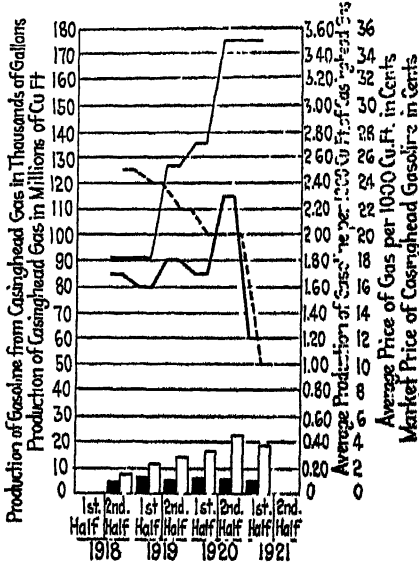
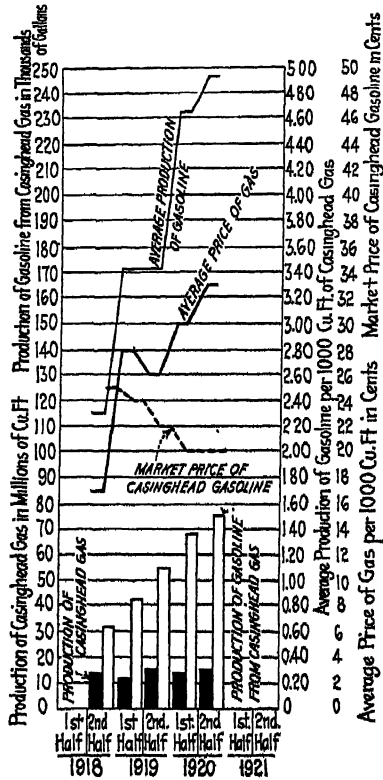
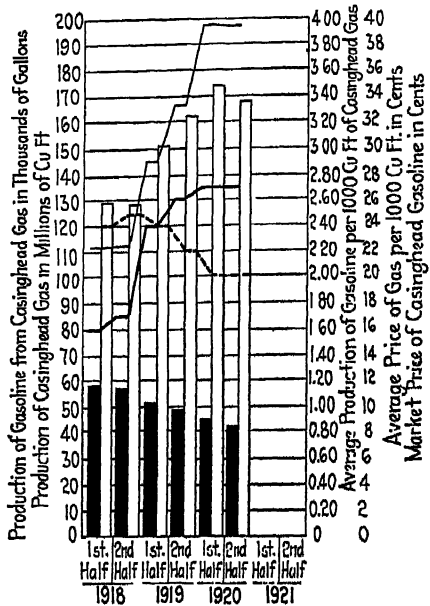
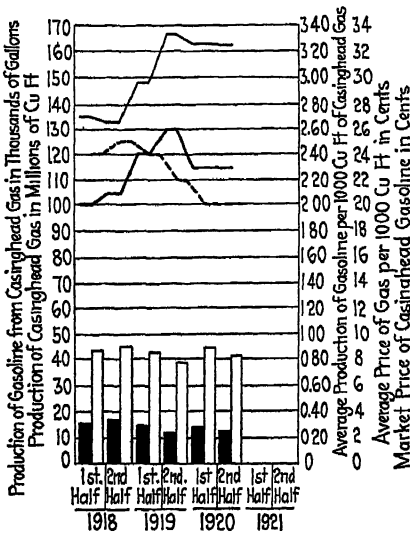


CASES 1, 2, AND 4.

Of all the districts from which data have been gathered, the Cushing field embraced in townships 17 and 18N, range 7E, is the youngest and also the most important from the standpoint of quality of oil produced, total production of oil per acre, and available reserves of casinghead gas. The operators in that field early realized the necessity of conserving the casinghead gas and, therefore, took every precaution possible in the opera-

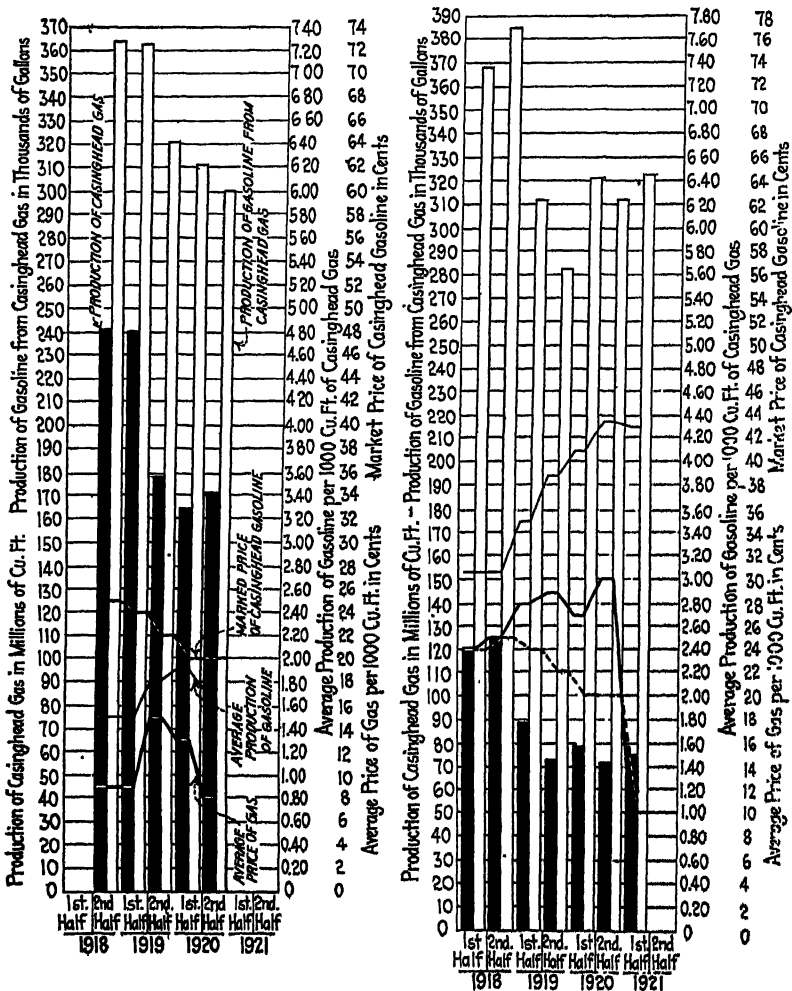


CASES 3, 5, 6, AND 8.



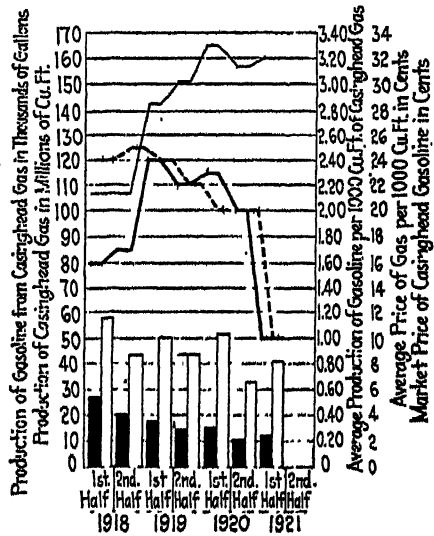
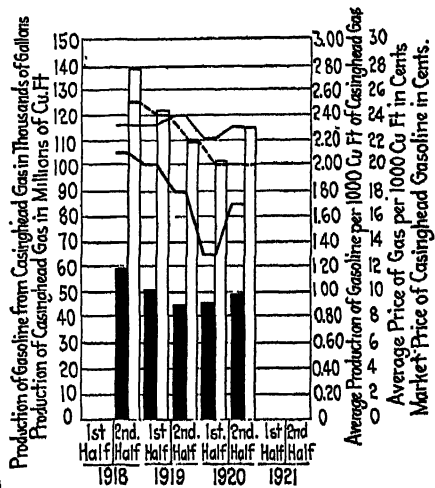
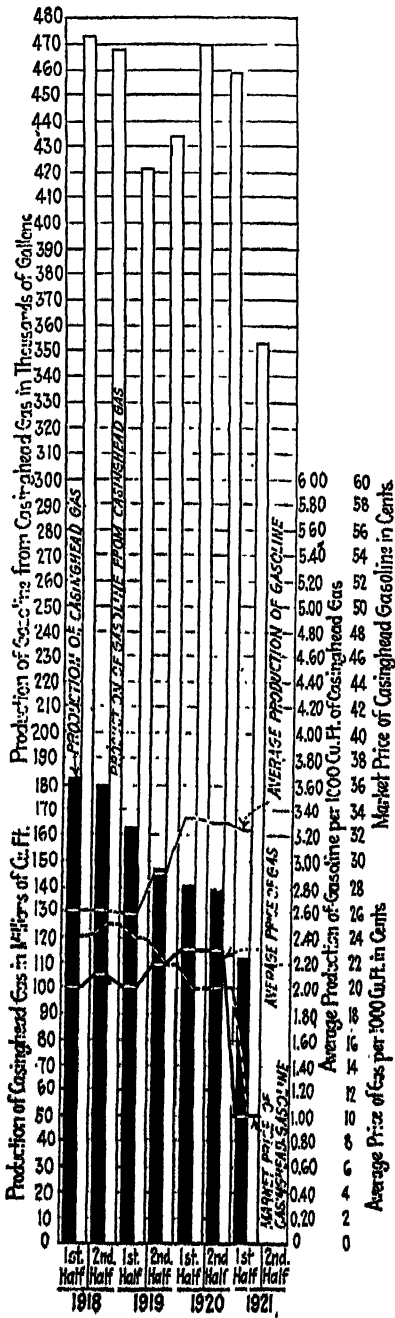
CASES 13, 14, 15, AND 16.

tion of the wells. The effect of the application of vacuum to the wells was carefully observed and charts were made showing relationship between quantity of oil produced, points of vacuum carried, productivity of gas, and related matters. Many producers postponed pulling a



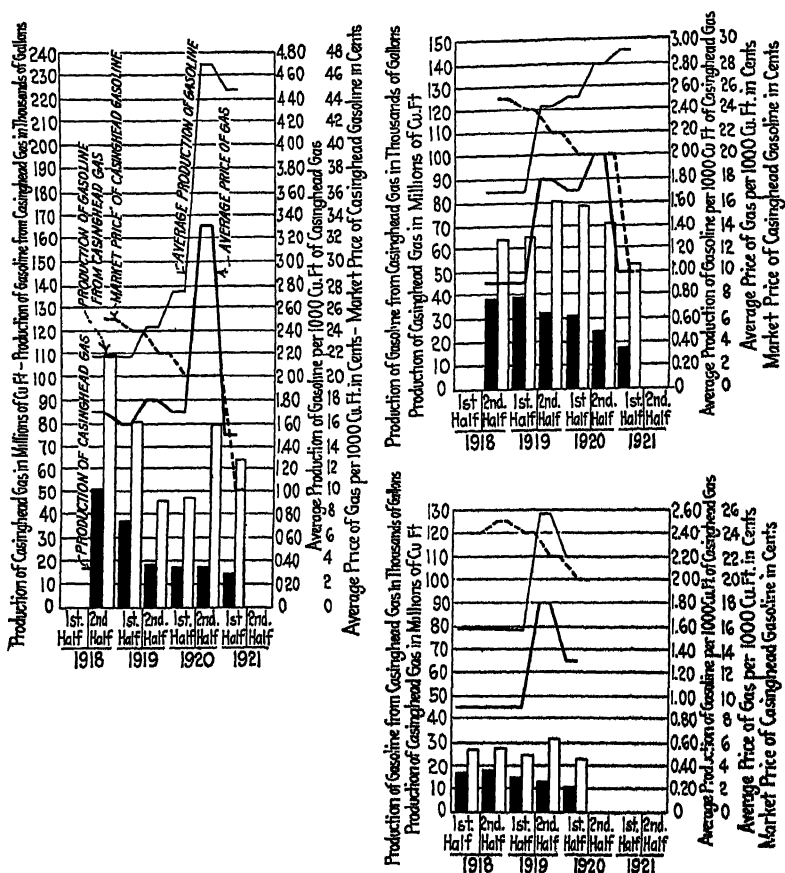
CASES 19 AND 20.

vacuum on their wells for several months, taking just enough gas to relieve the back pressure, or kept it at a point that would permit the maximum production of oil. This careful handling of the leases has no doubt resulted in a minimum depletion of the supply of casinghead gas in that field.





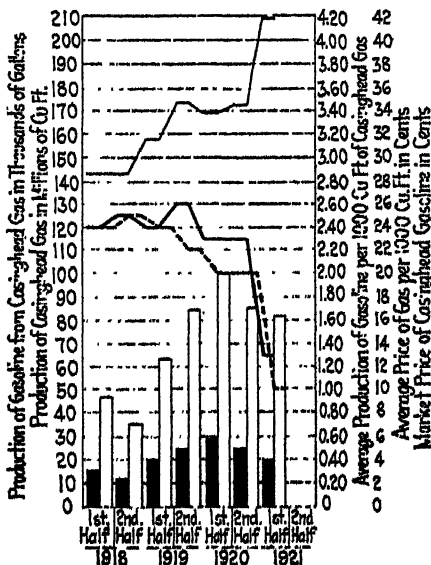
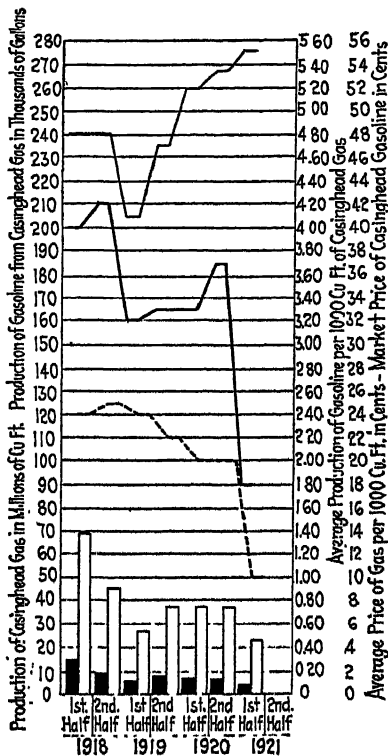
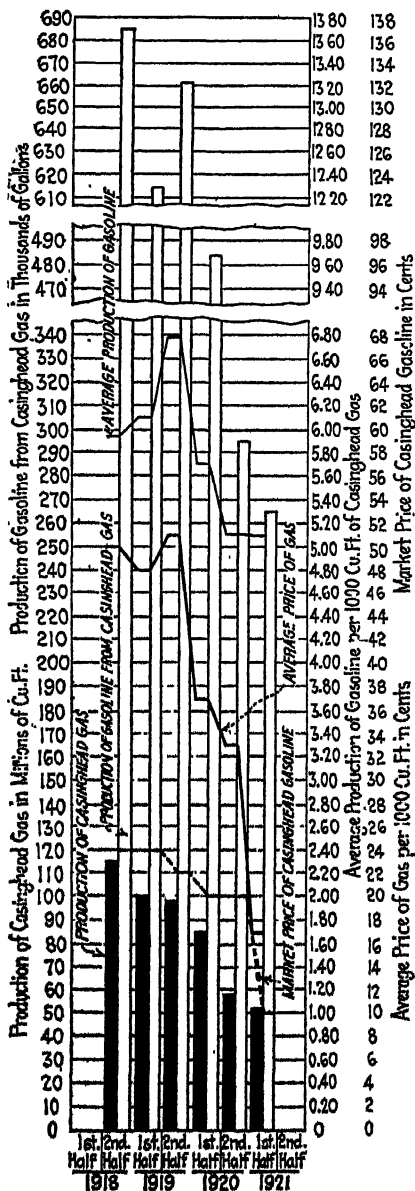
This preliminary presentation of the subject, from the standpoint of volumes of casinghead gas as closely as it was possible to determine them in field practice, considered in connection with the tests of productivity, confirms previous observations that the productivity of casinghead gas increases as the wells grow older but the rate of this increase is not so easily figured because of widely varying conditions. Following the usual



CASES 24, 25, AND 26.

law applicable to oil and gas production statistics, there is a gradual decline in the volume of casinghead gas from year to year, although the productivity increases.

In this record, the valuation factor obtained by the multiplication of the volume of the gas by its productivity, in gallons per thousand cubic feet, in order to obtain its potential casinghead-gasoline units, in gallons, shows an increase in fourteen of twenty-nine cases considered. In four cases, there is an increase in volumes because, possibly, of some irregu-



larity in operating conditions or measurements of gas; and in two cases the productivity of the gas averages slightly less on final test than on the initial test. While there has been an upward trend in the productivity figures in all but two cases, the total increase in productivity over the entire period has not exceeded  $1\frac{1}{4}$  gal. per 1000 cu. ft. except in cases 10, 14, 15, 16, and 24. In fourteen cases, the increase has been less than 1 gal. The greatest increase was in case 14, where the average productivity was raised 2.64 gallons.

These productivity tests are, of course, subject to the usual errors, such as: (1) Time of year taken, as climatic conditions will have a certain effect on tests; (2) operating conditions on the lease, whether wells are on or off the pump and cleaning out work; (3) the point at which the sample of the gas is taken; (4) inefficient testing equipment and poor connections; (5) small errors resulting from the limited quantity of gas tested; (6) evaporation in open-air tests.

Some of the tests were made by the owners of the leases and some by the purchasers of the gas, but in all cases there was a conscientious effort to arrive at as fair a field test as could be obtained. The tests have not been made at any particular time of the 6-mo. period under consideration as it was not possible to perform the work in that manner; but there is a 6-mo. interval between tests on each group of leases. There are sometimes considerable variations in the results of the productivity of gas from adjoining and nearby leases, but only the average has been taken for all the tests for each group of leases. Further, no records were obtained on the various percentages of air in the different systems connecting the wells with the casinghead-gasoline plants. This record, if it could have been obtained, would not have been dependable as it would have been changed from day to day, because of irregularities in operating conditions.

Many companies were testing out different methods of treating the gas; in fact at the inception of the industry few plants carried in their files any data on air tests. The practice of making regular and systematic tests for air content of casinghead gas is now followed in practically all modern plants and is an important factor in checking up leases.

Some manufacturers of casinghead gasoline check up the productivity tests of the casinghead gas on individual wells, sampling the gas under vacuum conditions at the mouth of the well. This is done to eliminate, as far as possible, the admixture and utilization of the poor grades of gas in the plants, as frequently one or two wells on an oil lease will produce gas inferior to that coming from the other producing wells on the property. Cutting out the wells making the poor gas is good operating practice as mixing and treating gas of different productivity will yield a quantity of gasoline below the average productivity of the casinghead gas mixed and utilized. Some plants have attempted to treat high and low grades of gas

in different units of the plant; this is not practicable unless large quantities of different grades of gas are available and facilities for segregation can be installed at minimum cost.

It is not claimed that the gasoline content, in gallons, as hereshown, represents the actual amount of casinghead gasoline that must be or was extracted and marketed in merchantable form. The procedure in making the tests, however, allows ample margin for evaporation and other losses in ordinary plant operations and, as far as this is the case, the number of gallons shown may be considered fairly representative of the value of the gas in gasoline that should be recovered in an efficient and well managed plant.

The evaluation figures, here set forth, showing the value of the casinghead gas at the wells and the value of the casinghead gasoline at the loading rack have been prepared merely as a matter of theoretical comparison. The value of the gas has been fixed in accordance with its productivity and in conformity with a schedule submitted to the Government by a number of producers of gas and manufacturers of casinghead gasoline in the Mid-Continent field and adopted and approved, Aug. 10, 1917. Subsequently, it was modified, the actual sale price of gasoline being substituted for the Chicago tank-wagon price. The market quotation per gallon is for raw casinghead gasoline of the ordinary grade suitable for use in blending operations.

For some time after the casinghead-gasoline business had reached its full development, the price of raw casinghead gasoline was above the market price of regular merchantable gasoline. There seemed to be a certain demand for this gasoline, as it was thought that it improved the regular gasoline when they were properly blended. It was also used with naphtha to make a different grade of gasoline. The trade soon learned, however, that casinghead gasoline did not possess many qualities claimed for it and the price declined below the market price of gasoline, known as the Chicago tank-wagon price. Since 1920, the average price of raw casinghead gasoline has ranged from 5 to 7 cents below that of Chicago tank-wagon quotation.

The average price of raw casinghead gasoline, as near as could be ascertained, has been used in these calculations; and when the actual average sale price is so used, the price of the gas works out on the basis of from 26.6 to 34.6 per cent. of the sale price of the gasoline per gallon. That is, if a casinghead gas tests 1 gal. of gasoline per 1000 cu. ft. and gasoline is selling at 15 cents per gallon, the price of the gas, according to the schedule, would be 4 cents, or 26.6 per cent. of the market price of the gasoline. It is conceded by all manufacturers of casinghead gasoline, who must purchase the casinghead gas, that the payment of from one-fifth, as a minimum, to a little over one-third, as a maximum, of the market price of 1 gal. of gasoline per 1000 cu. ft. of gas, in accordance

with the productivity of the gas, is equitable to all parties concerned. It is fully realized that richer gas can be handled at approximately the same expense as the poor grades of gas and, therefore, purchasers or users of the good gas can afford to pay a somewhat larger percentage of the value of the gasoline derived from the treatment of such gas.

The difference in value between the casinghead gas and the gasoline manufactured therefrom may seem somewhat large to one not familiar with the business. This difference, however, must take care of all manufacturing costs (the principal items of which are labor and supplies) including cost of the gas with additional charges for amortization of capital investment, upkeep, taxes, insurance, general and overhead expense, and yet afford a reasonable margin of profit.

That the casinghead-gasoline business as a whole is not as attractive a medium of investment as one would imagine is proved by the large number of dismantled plants and bankrupt gasoline companies in the Mid-Continent field. This statement is particularly applicable to those companies that must purchase their gas from producers at high prices and have made errors in estimating the available supply as well as quality of the gas to be used. There is considerable advantage in owning the oil leases and conducting operations thereon in the production of both oil and casinghead gas, using the latter in the manufacture of casinghead gasoline in one's own plants. Also when refineries producing blending material and possessed of adequate distributing and marketing facilities are owned and controlled by oil companies, the conditions are conducive to a substantial margin of profit. The purchase and the consolidation of many smaller plants into the larger operating groups has been an important development in the evolution of the casinghead gas industry during the past 2½ years. This has been due to the fact that these larger organizations, with ample capital and facilities for disposing of the casinghead gasoline, experience little difficulty in maintaining to the fullest efficiency every agency calculated to reduce the cost of manufacture, thereby increasing profits.

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## Effect of Back Pressure on Wells in Brock Field

By J. M. LOVEJOY,\* TULSA, OKLA.

(Tulsa Meeting, October, 1923)

VARIOUS estimates have been made as to the percentage of oil left in a field after the wells have become so small that it is no longer practical to produce them. Engineers have given the matter much study and can substantiate their figures by data taken from fields from the Appalachians to California. The average oil sand has a porosity of about 20 per cent., which gives a capacity per acre-foot of approximately 1500 bbl. The sand thickness in Oklahoma pools averages 20 ft. With 20 per cent. porosity and a 20-ft. sand thickness, the capacity per acre is 30,000 bbl., yet these pools will seldom yield more than 5000 bbl. to the acre.

These figures support the theory that at least 50 per cent. of the oil remains in a sand after all known methods to recover it have been used. Certainly we can never recover all the oil, unless in years to come oil becomes so rare and yet so necessary that the price will justify sinking shafts into the abandoned fields and regular mining methods of drifting and stoping. However, with improved methods of production and conservation of the natural agencies of expulsion, we should be able to increase recovery. It is with this in mind that this paper, relating to the effect of back pressure on wells, is presented.

Except in the fields where production is caused by hydrostatic pressure, the chief agency for getting oil out of the sand into the hole is the gas that occurs with the oil. After the pressure has declined, probably gravity also is a factor, but not an important one. With a given amount of oil in a sand and a given amount of gas occurring with the oil, the ratio of gas volume per barrel of oil is the key to the ultimate recovery from that sand. Our efforts should be along lines that will lower this ratio and make the gas, the agency given us by nature, do its work better and yield more of the oil, of which it is a part.

T. E. Swigart,<sup>1</sup> of the U. S. Bureau of Mines, has published an extract of the paper he is preparing under the title "The Effect of Back Pressures on Wells." The experiments described were made on two

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\* Division Manager, Amerada Petroleum Corpn.

<sup>1</sup> Amer. Assn. of Petrol. Geol., *Bull.* 7, No. 1.

small pumping wells in Osage County, Okla., and the results show a considerable reduction in the ratio of gas per barrel of oil by producing the wells against a back pressure. Although Mr. Swigart's work with back pressures is the only information on this subject that has been published, other tests made with back pressures against flowing wells have not only failed to show a reduction in gas ratio but show an actual increase in this ratio. The Mid-West Refining Co. conducted a series of tests on flowing wells in the Salt Creek field, under the direction of E. L. Estabrook, which showed that straight back pressures did not lower the gas volume per barrel of oil.

T. F. Morgan, in the September, 1923, number of *Mining and Oil Bulletin of California*, says:

Restriction of oil production has undoubtedly assisted greatly in the conservation of gas, while its general effect has been to increase the ratio of gas to oil.

This applies to the large flowing wells in the fields of the Los Angeles basin.

The experiments to be described in this paper confirm the conclusions of Mr. Morgan and Mr. Estabrook, as applied to small wells. Possibly the reason for the difference between these results and those of Mr. Swigart is that he was working with pumping wells only, while pumping and flowing wells are combined in these tests.

### BACK PRESSURES

The experiments were carried out in the Brock Field in township 5 south, range 1 east, Carter County, Okla., about 9 miles southwest of Ardmore. The field was discovered in January, 1920, and has been developed slowly, now having thirty producing wells. All the productive leasehold is owned by the Amerada Petroleum Corp'n. As the company operates a casinghead-gasoline plant in the field, means were available for metering the gas from separate wells, separate leases, and the entire field.

The production comes from a series of sands in a shale-and-sand zone found from 1300 to 2000 ft. The average thickness of the sands is about 20 ft. and the average initial production of the wells about 45 bbl. The sand is fine-grained and compact but not very hard. Only two wells in the field have been shot; shooting caused the sand to continue caving into the hole to such an extent that it required weeks to clean out and no benefits in production were obtained.

Back pressures were first applied, to some of the wells, by maintaining 15 lb. back pressure on a Ballard trap, the gas from the trap being used for drilling purposes. As the back pressure did not affect the production of the wells in the trap, it was decided to try higher pressures and

measure both oil production and gas volume. At this time, most of the wells were flowing through tubing set with a packer; a few were flowing through casing and some were pumping. Each well was then equipped with a spring release valve that could be set for any pressure desired and a pressure gage was attached to the lead line from each well.

The results of the various back pressures used have been recorded from Jan. 1 to Sept. 15. The curves, Fig. 1, show that, during January, by building up pressures of 15 lb. and later releasing the back pressure entirely, there was little effect on the wells. In the period beginning

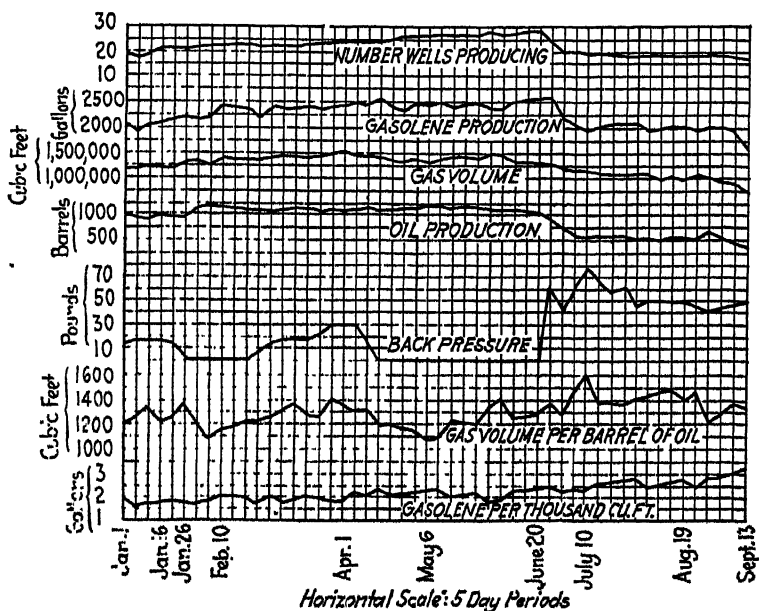


FIG. 1.

Feb. 10, with no back pressure, there is a gas ratio of 1160 cu. ft. per bbl. On April 1, with a back pressure of 32 lb., the ratio was 1320 cu. ft. per bbl. On May 6, with no back pressure, the lowest ratio of the series of tests was recorded, being 1070 cu. ft. per bbl.; the highest ratio is in the period beginning July 10, when with a back pressure of 76 lb., 1620 cu. ft. of gas was required to produce a barrel of oil.

The higher back pressures, shown after June 20, were not applied purely in the interests of science but because pro-rating became effective at this time and it was necessary to curtail production.

It is interesting to note the generally higher gasoline content per thousand cubic feet of gas during the last two months of the tests, with the wells producing against about 50 lb. back pressure. This may be partly accounted for by the fact that during the very hot weather gas



lines were connected with the roofs of two 55,000-bbl. tanks full of oil and undoubtedly some very rich gas came into the plant from these tanks. However, we believe that a back pressure does increase the percentage of gasoline in the gas to some extent. The specific gravity of the oil did not appreciably vary with the back pressure.

Date, Average 5 Days Beginning	Number of Flowing Wells	Number of Pumping Wells	Average Back Pressure, Pounds	Total Oil Production, Barrels	Total Gas Volume, 1000 Cu. Ft.	Gas Vol- ume per Barrel of Oil, Cubic Feet	Gasoline Content per 1000 Cu. ft. Gas, Gallons
Jan. 1.....	15	4	12	950	1,150	1220	2.0
Jan. 16.....	14	6	15	975	1,150	1220	1.74
Jan. 26.....	14	6	0	925	1,300	1300	1.82
Feb. 10.....	16	6	0	1200	1,375	1160	2.01
Apr. 1.....	17	8	32	1100	1,500	1360	1.91
May 6. ....	17	9	0	1160	1,320	1070	2.27
June 20.....	18	10	0	1005	1,275	1270	2.40
July 10.....	19	0	76	510	850	1620	2.30
Aug. 19.....	18	0	48	500	720	1400	2.70
Sept. 13.....	16	0	49	350	490	1320	3.15

The average back pressure shown in the curves is simply a mathematical average; with an average pressure of 50 lb. some of the wells had as high as 90 lb. and others as low as 15 lb. After the pumping wells were shut down in July, they were left connected to the traps and made a small amount of gas.

The back-pressure system of curtailing production has proved very satisfactory. The oil production desired can be controlled almost to a barrel by regulation of the back pressure. Frequent tests have been made to ascertain whether or not the wells were being damaged by the heavy back pressures. In all cases, when all pressure was removed, the wells responded with the full production that they had previously been making under open flow.

#### STOP-COCKING

Preliminary experiments made by H. C. George, of the U. S. Bureau of Mines, on wells in this field with the stop-cocking method of producing gas, show satisfactory results, and at his suggestion further tests are being carried on. By this method, the well is completely closed until its maximum pressure is built up. It is then opened and, as the pressure rapidly goes down, a small flow of oil will follow. The valves are then closed again and the operation repeated.

An apparatus has been devised by Mr. Bach, of the Amerada Petroleum Corpn., which automatically opens and closes the valves at the

proper times, so that a continuous operation is possible. The results of the tests already made are encouraging and we trust that further work with this method will show as good results.

From Sept. 1 to 20, inclusive, well flowing through tubing and with no back pressure,

Gas passed.....	554,500 cu. ft.
Oil produced.....	551 bbl.
Average daily oil production.....	27.5 bbl.
Gas per barrel of oil.....	1006 cu. ft.

From Sept. 21 to 25, inclusive, with apparatus attached allowing well to flow entirely open each time a pressure of 50 lb. was reached,

Gas passed.....	129,405 cu. ft.
Oil produced.....	155 bbl.
Average daily oil production.....	31 bbl.
Gas per barrel of oil.....	834 cu. ft.

Not only was the gas volume of oil decreased by 172 cu. ft. per bbl., but the actual production of the well was increased from 27.5 to 31 bbl.

The well would make two flows about 20 min. apart and then would not flow again for nearly 2 hr., although in some cases during the 2-hr. period the well would build up enough pressure to cause the valve to release but would not be followed by a flow of oil. This well was equipped with 3-in. tubing. It is thought that even better results will be obtained by this method from wells equipped with 2-in. tubing.

### CONCLUSIONS

The writer hesitates to present conclusions. It is difficult to believe that back pressure on flowing wells is a waste rather than a conservation of natural forces. Yet this is the result of our tests on straight back pressures, although the tests on the stop-cocking method give encouraging results. It is hoped that more work will be done along these lines and that true conservation and consequent methods of increasing the ultimate recovery will soon be discovered.

### DISCUSSION

W. I. ESTABROOK,\* Casper, Wyo. (written discussion).—This subject is part of the general problem of the efficient utilization of the lifting power of gas in oil wells, the study of which is likely to lead to increased recoveries of oil from sands with greatly decreased costs of production. That the author's results do not coincide with those of other investigators illustrates a fundamental difficulty in generalizing on this problem. Every oil well is individual; it varies from every other well in the amount and relative proportions of oil and gas being produced, as well as in rock

\* Petroleum Production Engineer, Midwest Refining Co.

pressure, sand conditions, offset wells, etc. The size of the casing or tubing through which the well is produced, the size of the flow nipple, the location of the packer, the location of the perforations through which the oil and gas enter the tubing also affect the results in such tests.

The studies that have been made indicate that we need to know much more about the various conditions that affect the efficiency of the use of the lifting power of the gas in a producing oil well. We need descriptions of the visible evidences of efficient and inefficient production so that field methods may be improved without the necessity of metering the gas or measuring the pressure of every oil well. Probably all will agree that a steady stream of oil completely filling the opening through which it flows, and permitting the escape of no undissolved gas, represents the most efficient utilization of the gas of a flowing well. This standard may be easily attained in certain wells but is difficult, or perhaps impossible, with others in which the natural proportion of gas to oil is higher. In the Salt Creek field, some wells produce as little as 400 cu. ft. of gas per barrel of oil, while in others it has not been possible to reduce the gas volume below 2000 cu. ft. per barrel.

H. C. GEORGE,\* Ardmore, Okla. (written discussion).—From experiments with back pressure and stop-cocking wells in the Brock field, I conclude that the more favorable results secured by stop-cocking, as compared with constant back pressure, were due to the fact that with stop-cocking the wells were entirely closed in more than half of the time, so that no gas escaped; when the well was opened, the release of pressure usually resulted in a flow of oil with the gas. On the other hand, when the back-pressure valve was set for a given pressure, much of the time gas was escaping through the valve without being accompanied by a flow of oil. By both of these methods, as used at the Brock field, the oil flowed by heads.

The use of flow nipples, or the use of tubing of only sufficient internal sectional area to accommodate the oil production by continuous flowing, would have shown a still lower production of gas per barrel of oil than either of the methods used. This belief is not based upon any experiments that I have made but on the results observed at flowing wells in Pennsylvania where 1¼-in. tubing was used, results observed at several large wells in the Mid-Continent flowing continuously for a period of several months, and the use of flow nipples in some of the large wells of California.

In oil-field practice, that size of tubing used in a flowing well invariably has been of the size that the operator expected to use later for pumping the well. This has been the main consideration in making the installation of tubing at the flowing well, and has in most cases resulted in the use of tubing too large for the flowing well.

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\*Petroleum Engineer, U. S. Bureau of Mines.

## Trend of Prices in the Petroleum Industry

By JOSEPH E. POGUE,\* NEW YORK, N. Y.

(New York Meeting, February, 1924)

THE prices of crude petroleum and its derivatives have shown an upward trend from 1915 to 1920, and a downward trend from 1920 to 1923, see Table 1. Over the former period, oil prices were dominated by the rapidly increasing demands and inflation incident to the war and its aftermath, while over the latter period oil prices were influenced at the outset by deflation and then by the conditions of overproduction that have characterized the past three years. The purpose of this paper is to analyze the broader features of the more recent price movements in the petroleum industry and to relate these features to basic economic conditions in the industry.

### INDEX NUMBERS OF OIL PRICES

The analysis and comparison of price movements may be facilitated by converting actual prices into relative prices, or index numbers, with 1913 taken as a base of 100. In this way, the various price groups are expressed as percentages of the 1913 prices and may thus be readily compared with one another or with the average prices of other commodities similarly expressed.

Table 1 gives the index numbers representing the average prices of crude petroleum, gasoline, kerosene, fuel oil, lubricating oils, and all commodities. The last named is the index of all commodities as published by the U. S. Bureau of Labor Statistics and is widely accepted as the official measure of the general price level. The index numbers of oil prices were calculated by the writer from weekly quotations published in trade journals.

Fig. 1 shows in graphic form the trend of oil prices by months over the period 1920-23. It may be observed that the prices of crude oil and its derivatives move in rough conformity with one another; tend to follow

\* Consulting Engineer, New York.

broadly the course of the general price level; and show a sort of cyclical movement—down, up, down, up, down—over the four-year period. The chart illustrates clearly the drastic decline in oil prices that characterized the last three quarters of 1923, following the period of advancing prices in the first quarter. Attention is directed particularly to the drastic fall in gasoline prices in 1923, the price of this commodity reaching a level far below the low point of 1921.

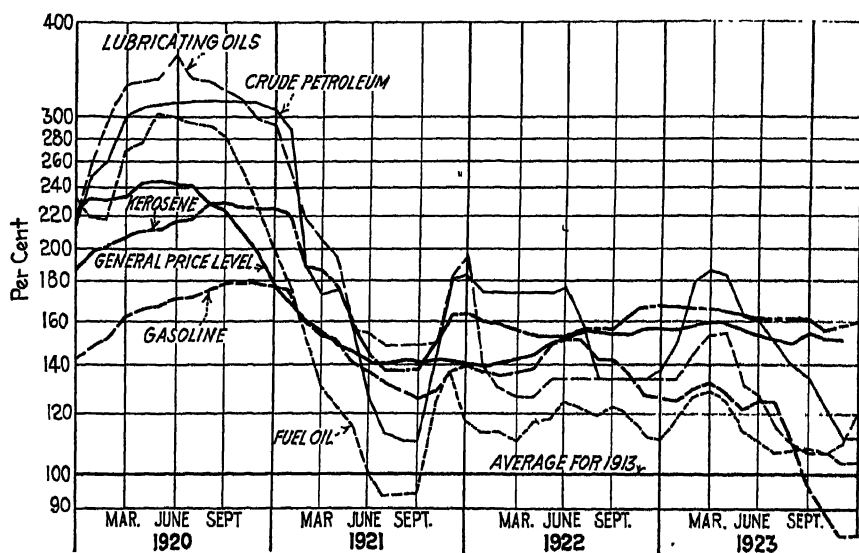


FIG. 1.—TREND OF RELATIVE PRICES OF MINERAL OILS IN UNITED STATES, 1920-23.

#### DEVIATION OF OIL PRICES FROM THE GENERAL PRICE LEVEL

The price levels shown in Table 1 and Fig. 1 result from two sets of causes, the one arising from conditions within the oil industry, and the other from variations in the general purchasing power of the dollar. In order to eliminate the latter factor, the index numbers of oil prices were divided by the index numbers representing the general price level, and a new set of figures was obtained expressing oil prices in percentages of the general price level. These figures were then plotted by months for the period 1913-23, with the results shown in Fig. 2.

Study of Fig. 2 will reveal the cyclical character of the price movements in their broader aspects. In the 11-year period covered by the chart, there were six broad downward movements and five upward movements. Thus five and one-half cycles were described. The more recent cycles were briefer in duration than the earlier ones. At the close of 1923, prices were at the bottom of a cyclical movement. In the past, such a position was invariably followed by a major upswing.

## OVERPRODUCTION OF CRUDE OIL, 1921-23

The dominant factor in oil prices during the past four years (aside from the general deflation that affected all prices in 1920 and 1921) was

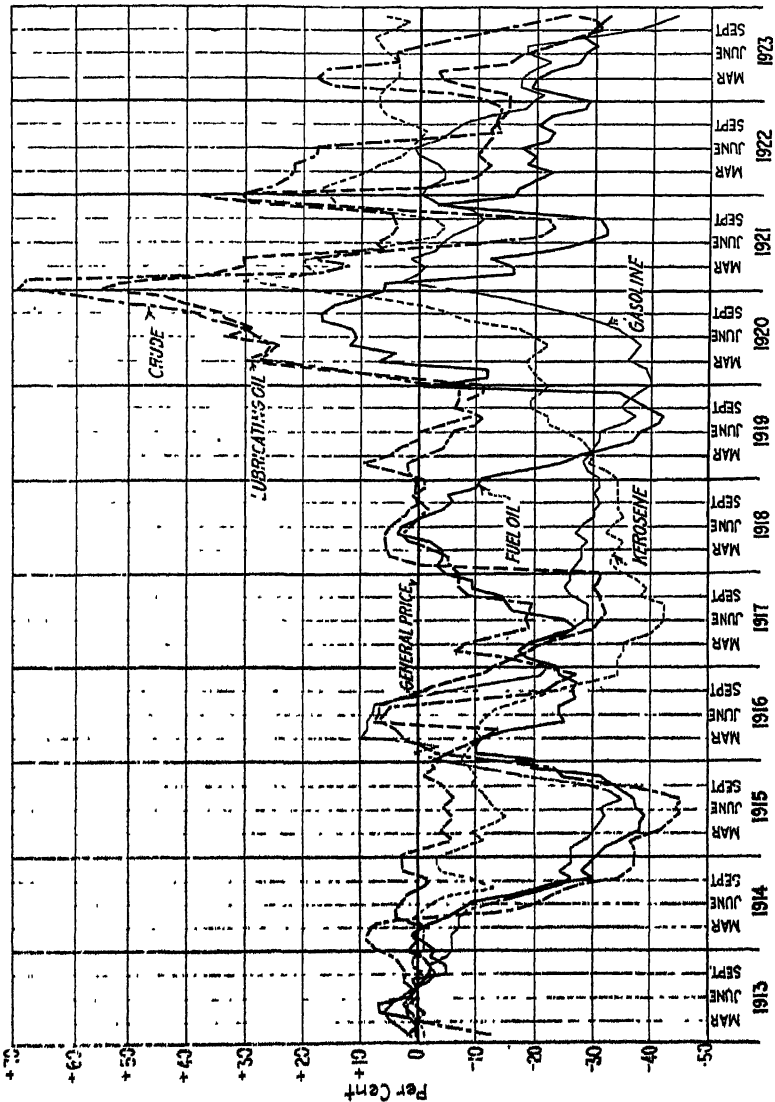


Fig. 2.—DEVIATIONS OF OIL PRICES FROM GENERAL PRICE LEVEL, 1913-23.

the almost unbroken state of overproduction that beset the industry over this period. The degree and variation of this condition of overproduction are shown in Fig. 3, in which the daily rate of additions to or

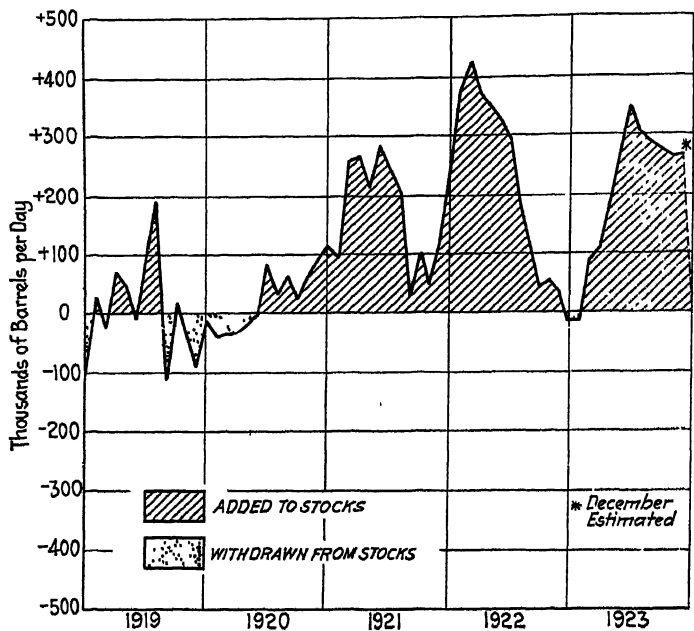


FIG. 3.—DAILY RATE OF CHANGE IN CRUDE-OIL STOCKS IN UNITED STATES, 1919-23.

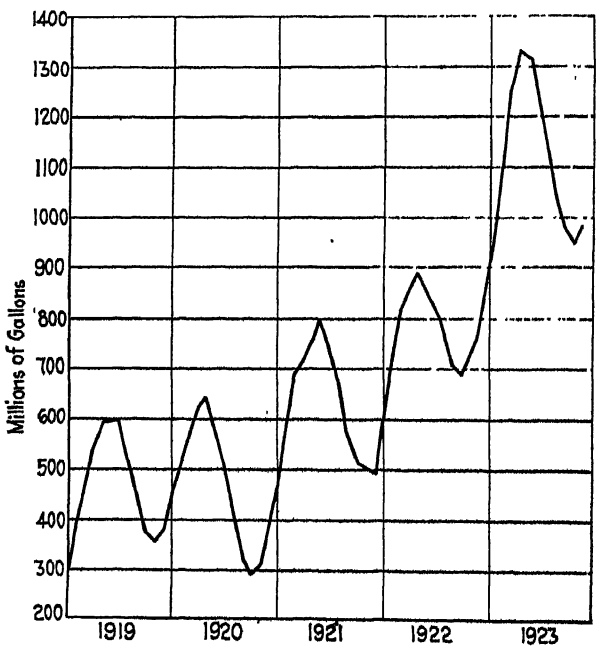


FIG. 4.—TREND OF GASOLINE STOCKS IN UNITED STATES, 1919-23.

withdrawals from crude-oil storage are shown by months for the period 1919-23. It may be readily seen that from the middle of 1920 until the end of 1923 there was practically a continuous addition to crude-oil stocks, with a period in the fall of 1921 when a sharp drop in the rate of addition to storage took place, and a period at the close of 1922 where there was a brief and slight withdrawal from stocks. These two periods were followed by general price advances (see Figs. 1 and 2), while the intervening time was marked by declining prices. Again, during December, 1923, the rate of additions to crude-oil storage decreased sharply as a result of declines in flush production in the Sante Fé Springs and Powell pools, and this change was followed almost immediately by the beginning of an upturn in oil prices. Without resorting to further details, the conditions of crude-oil supply and demand depicted in Fig. 3 afford an explanation of the broad movement of oil prices over the past few years.

#### OVERPRODUCTION OF GASOLINE IN 1923

The price of gasoline suffered a severe decline in 1923, reaching 84 per cent. of its pre-war price (see Table 1 and Fig. 1). If corrected for the difference in the purchasing power of the dollar, the price of gasoline in 1923 reached the lowest level attained in the past 11 years. (See Fig. 2.) The explanation of this severe decline lies in the overproduction of crude oil coupled with the overproduction of gasoline. The extent of the oversupply of gasoline in 1923 is clearly indicated by Fig. 4, which shows by months the level of gasoline stocks in the United States. The abnormal rise of gasoline stocks during the first third of 1923 is apparent at a glance. It is noteworthy that stocks of gasoline became excessive before the price of crude oil collapsed as a result of the overproduction of this raw material, particularly in the flush pools of California. Therefore an oversupply of gasoline in the winter of 1923 must share with an overproduction of crude oil the responsibility for the price débâcle of 1923.

#### BUNCHING OF FLUSH POOLS IN 1923

The year 1923 was characterized by the bunching of a large number of large oil-pools. During the 60-odd years of the American petroleum industry, there have been 16 oil-pools that have attained a maximum daily rate of output exceeding 100,000 bbl.; and of these 16 pools, 8 reached their peaks within a period of seven months in 1923.<sup>1</sup> (See Fig. 5.) This telescoping of flush production was the primary factor underlying the condition of overproduction that led to the price declines of 1923,

<sup>1</sup> A theory to account for this phenomenal bunching of flush pools is given by the writer in a paper entitled "The Bearing of Improved Technique Upon the Production of Petroleum in the United States," presented before the American Statistical Association on Dec. 28, 1923.



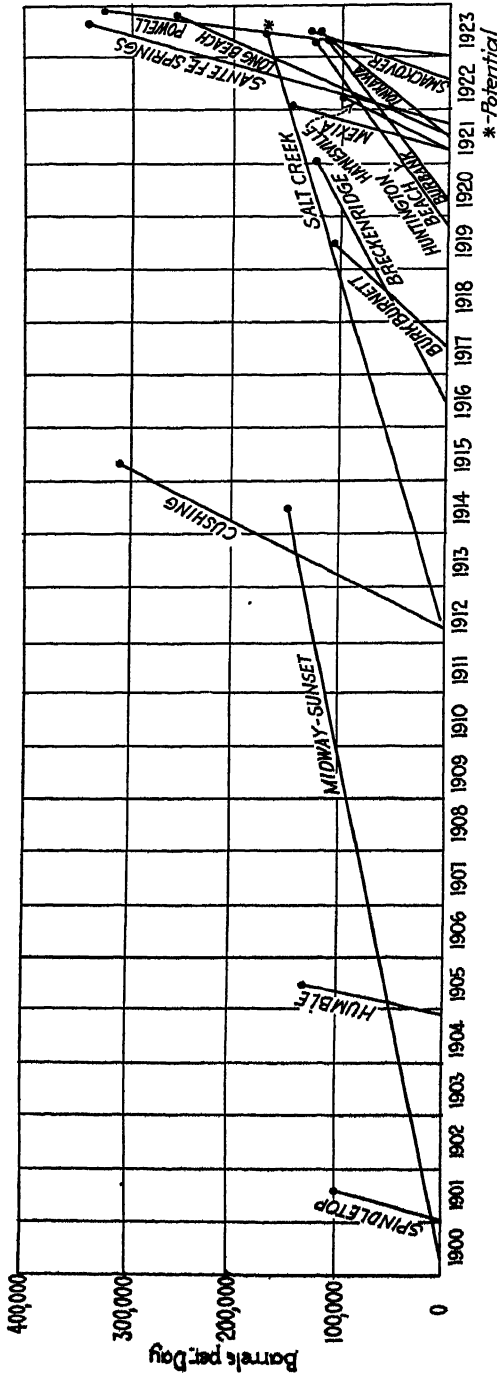


Fig. 5.—CHART SHOWING DATES OF DISCOVERY AND PEAK PRODUCTION OF ALL OIL-POOLS IN UNITED STATES WHICH HAVE REACHED A DAILY RATE OF OUTPUT EXCEEDING 100,000 BBL.

and contrariwise is the occasion of the recent sharp drop in production which has initiated a new upward move in oil prices.

TABLE 1.—*Trend of Relative Prices of Crude Petroleum and Its Derivatives in the United States, by Years from 1913 to 1923 Inclusive, and by Months, 1922 and 1923*

(Prices in 1913 = 100)

	Crude Petroleum at Wells	Gasoline, Tank Wagon	Kerosene, Tank Wagon	Fuel Oil at Refinery	Lubricating Oils Jobbing Quotations	All Com- modities
<b>By years</b>						
1913.....	100	100	100	100	100	100
1914.....	83	83	97	85	101	98
1915.....	66	75	90	68	97	101
1916.....	117	121	101	98	119	127
1917.....	155	132	108	147	126	177
1918.....	195	139	130	189	200	194
1919.....	197	142	162	140	209	206
1920.....	302	170	217	262	318	226
1921.....	163	143	164	122	170	147
1922.....	156	140	158	117	132	149
1923.....	150	112	163	113	125	
<b>By months</b>						
<b>1922</b>						
Jan.....	174	137	161	114	140	138
Feb.....	174	135	159	113	120	141
Mar.....	174	136	155	110	126	142
Apr.....	174	139	153	117	126	143
May.....	174	148	153	118	133	148
June.....	177	151	153	124	133	150
July.....	160	151	156	121	133	155
Aug.....	183	142	154	119	133	155
Sept.....	133	142	156	122	133	153
Oct.....	133	136	163	118	133	154
Nov.....	134	128	167	113	133	156
Dec.....	138	127	167	111	133	156
<b>1923</b>						
Jan.....	148	124	167	118	133	156
Feb.....	179	129	166	126	144	157
Mar.....	187	132	166	128	153	159
Apr.....	185	128	165	124	154	159
May.....	163	121	163	114	133	156
June.....	160	125	162	110	127	153
July.....	149	124	162	106	116	151
Aug.....	140	110	162	108	110	150
Sept.....	135	97	162	108	107	154
Oct.....	123	90	156	106	107	153
Nov.....	118	84	158	103	110	152
Dec.....	112	84	160	103	119	

## PRICE TREND FOR 1924

This analysis has shown that oil prices move in cycles and that the close of 1923 saw oil prices at the bottom of a sharp downward movement which had brought prices to levels approximately equaling the lows of previous major down-swings. Low prices usually correct the conditions that cause the declines, so that advancing prices follow. The year 1923 came to a close with oil prices in a technical position for an upward movement, and this tendency was given free play by the sharp drop in production resulting from the synchronous decline of eight major flush pools. It is probable that we are now in the presence of a major upswing in the prices of crude petroleum and its derivatives.

## DISCUSSION

E. DeGOLYER, New York, N. Y.—An extremely large part of our production has come from big flush pools. If a field attained 80,000 bbl. per day, it was big flush production just as much as if it reached the 100,000 bbl. mark. At the time we reached our maximum production last year, in the week ending Sept. 8, when the daily production was about 2,250,000 bbl., more than half the production was coming from the eight flush pools.

The whole point to that is, that in order to maintain even what might be called a more or less normal production, we must have continual replacement of pools passing from their flush stage by the discovery of other pools that develop into flush pools of great importance.

It is extremely important to us whether these pools are found by luck or by skill or a mixture of both. If they are found by luck, that is if their development is more or less accidental—I do not agree with the idea recently expressed by several that we find all these flush pools because we have greatly developed our technique of oil production—if it is more or less of a coincidence, it is pretty certain that we are not going to have a bunching of pools like this again in the near future. The laws of probability and chance are strongly against it. If these pools are found as a result of skill we should have continued overproduction for some time to come.

Undoubtedly both luck and skill have their effect. Improved technique, the ability to locate wells better and to drill them to constantly greater depths certainly has a great deal to do with these flush pools. Many of them could not be drilled without this improved skill, but improved technique in finding these flush pools is something about which I am not certain.

Take the eight flush pools mentioned, which caused the trouble last year. No group of unprejudiced oil geologists will maintain that they were discovered by reason of any marked advance in geologic ability;

in other words, the discovery was largely accidental. Take the three fields (Huntington Beach, Long Beach, and Sante Fé Springs) in the Los Angeles basin; after going there last fall, seeing the geology, and learning what the California men had to say about the surface geology, I believe that the discovery of the fields was rather a daring piece of wildcatting. I doubt very much whether the average man would put his money into a similar proposition if one were able to take it to him tomorrow; that is, a big hill in the midst of a basin of comparatively recent deposits. At Tonkawa, in Oklahoma, the southern end of the pool is well expressed geologically; the northern end runs off into the flood plain of the river and there is no surface geology. That is not really important as the discovery was made on the southern end, and as the geology is well expressed there, we might give Tonkawa 100 per cent. as a geologic prospect in advance. Burbank and Smackover are not indicated on the surface. There is a little structure at Burbank, where the discovery well was drilled for gas, but there is no inviting structure with parallelism of surface and subsurface beds. There is no indication of the pool as it afterward developed; it was a matter of sand condition and not a matter of structure. At Smackover, I do not believe anybody knew what the structure was. Powell is another place where there is some geologic expression, but it was rather thin. I always refer to it as a type of field that is better explained geologically after it has been discovered by a wildcatter.

So, to my mind, the bunching of these fields is more of a casual occurrence than the result of an improved technique in oil finding. I do not mean that no credit is due to the improved technique in oil finding nor that there is none due to improved drilling technique, but I do not think the picture presented by these flush pools justifies any strong claims as to our ability to go out and find more pools like them.

C. W. HAMILTON, New York, N. Y.—It seems to me that the author should include the possible influence of foreign production in his interpolation of the trend of prices in the petroleum industry. He has brought out clearly the effect of bunching of peak production for the bonanza pools of the United States, but he has not taken into consideration the trend of oil production in Mexico, which has had some bearing on the crude market in past years. At the present time, one field in Mexico is producing more oil per day than any single field in the United States.

JAY A. CARPENTER, Los Angeles, Calif.—I would like to take exception to the statement concerning the Long Beach, Sante Fé, and Huntington Beach fields. The original discovery of those fields was not made by wildcaters, but by men of such companies as Standard Oil and Union Oil, who are able to drill the wells 5000 ft. deep and take the law of average for their profit. Our overproduction has been from the promoter type, who follows into the field, draining it too rapidly.

E. DEGOLYER.—I think my remarks have been misunderstood. I did not want to maintain that the discovery was the result of stock speculation. I am always ready to defend the statement that a large number of our fields are found on the basis of capital loss. The wildcatter—the little syndicate that goes out and puts \$30,000 or \$40,000 (or whatever it can get together) into a venture, and drills a wildcat well, and in ninety-nine cases out of one hundred loses its money, has a function and performs it. As far as the promoting type is concerned, I had no reference to that at all.

I realize that the geologist must go farther afield in speculative fashion. No man can wait until he finds an anticline like Cushing in Oklahoma; men are going out and drilling on poorer evidence all the time. They are approaching more nearly the type of operation of the old wildcatter. As they are exhausting possibilities, they are coming closer to going out and drilling wells, as has been so well expressed, on the law of averages. There is no question but that a good deal of oil production can be built up on that basis. The oil industry ran for a long time almost altogether on that basis, and some important oil companies have been built up altogether on that basis.

H. A. WHEELER,\* St. Louis, Mo.—This paper clearly brings out the extreme importance of these eight major pools that are of so very recent discovery. If you will look back ten years you will recall that 95 if not 99 per cent. of the oil companies looked on geologists as "doodle-bugs;" and even today over 75 per cent. of the oil operators east of the Mississippi, who are old oil men born and brought up in the business for one or two generations, still look upon geologists as "doodle-bugs." It is certainly significant that since the oil geologist has been recognized and appreciated by financiers and progressive operators, we have had this most phenomenal bringing in of eight bonanza pools.

While the geologist must sometimes take considerable risk, when he can only obtain fragmentary evidence that is not conclusive, and consequently sometimes fails, he has been responsible for opening up many new oil pools and he will make Colorado our next big producer, which up to three months ago was one of the worst graveyards in the past 40 years. The recently discovered Wellington dome was drilled ten years ago on a structure that I understand is self-evident, but they did not go deep enough. When first drilled, we did not realize the great depth of the sand and outside of California a well over 4200 ft. deep was regarded as impracticable. Since then we have greatly advanced in our technique and capital is willing to finance these costly "wildcats." I think geologists are entitled to more credit than our chairman suggests.

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\* Consulting Engineer.

There is one thing that I want to mention in connection with this paper. The author showed a rapid increase in gasoline stocks, but our consumption was 20 per cent. greater last year than ever before. If we turn out 4,000,000 automobiles this year, or the same as last year (and some have estimated as high as 5,000,000) and as there are over 15,000,000 registered cars, we are going to run into a heavy shortage of oil next year, if not before the end of this year, unless two or three new gusher or bonanza pools are discovered.

It is going to be extremely interesting to see whether that hiatus will occur, or whether a good many of the areas will be opened. As it seems highly improbable that the unparalleled discoveries of the past three years will be duplicated, the outlook for future prices for crude oil is very encouraging.

## The Law of Supply and Demand

BY ARTHUR KNAPP, PHILADELPHIA, PA.

(New York Meeting, February, 1924)

THE law of supply and demand is, in general terms, that law which governs the price of any commodity in an unrestricted competitive market. There are several variables which, for the purpose of this discussion, will be defined only as they apply to the petroleum industry:

*Production:* The volume of petroleum that is moved from leases.

*Stocks:* The volume of petroleum that is in the hands of the tank farm and pipeline companies.

*Inventory:* The value of the stocks at the market.

*Consumption:* The indicated delivery of oil to others than those who hold stocks.

*Demand:* The potential absorbing power of the consuming market. Demand is the expression of the needs of the consumer and may depend on the economic value of the oil to the consumer. In times of low prices, the demand is the same as the consumption but during periods of high prices or deficiency in supply, the demand may be greater than consumption.

A general expression of the law is as follows:

Some relation between	production	}	and	{	consumption	controls price
	or				or	
	stocks				demand	
	or					
	inventory					

### THE LAW AS APPLIED TO CRUDE-OIL MARKET

The above general expression of the law shows that there are six relations between variables that must be investigated in any attempt to establish the exact status of price control at any time.

#### *Production vs. Consumption*

If stocks of crude oil were very low, so that the flow of oil to the market was directly from the producer to the consumer and not, in a large measure, through stocks, some relation between production and consumption would be proportional to price changes. We have no criterion whereby we can tell, at present, what volume of stocks and production

would bring about this phase because this condition has not existed since the early days of the industry.

The increases in crude prices that occurred in January, 1924, were due to the influence of a decrease in production but not because of the volume of production. This price increase is largely due to the anticipation that there will be a draft on stocks.

### *Stocks vs. Consumption*

Many attempts have been made to apply the expression, "Stocks  $\div$  Consumption = Days' Supply," as being the expression of the law of supply and demand under the present conditions. If a simple ratio between the volume of stocks and the volume of consumption expressed the law, there should be some similarity between the curve of this ratio and the curve of price. There is no close economic relation between "days,

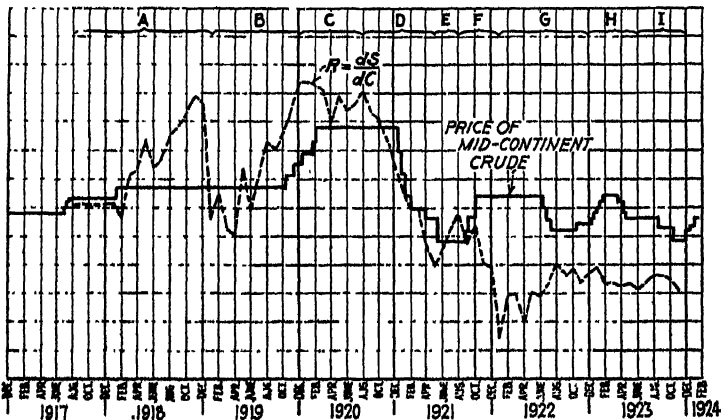


FIG. 1.—RATIO OF RATE OF INCREASE OF STOCKS TO RATE OF INCREASE OF CONSUMPTION.

supply" for any two periods hence it is not an expression of the law of supply and demand. Certainly the economic relation between 2 days' supply and its corresponding consumption and price and 200 days' supply and its corresponding consumption and price is not expressed by the ratio of 2 to 200. When stocks become so low that days' supply has any economic significance, then production would have more effect on price than would the volume of stocks.

Consider, however, not the ratio of the volumes of stocks and consumption but the ratio of the rate of change between the two. Let  $dC$  represent the rate of change of consumption from month to month and  $dS$  the rate of change of stocks for corresponding periods. Then  $R$ , or the ratio of the rates of change, is  $dS \div dC$ . The relation between a curve



of the expression  $R = dS \div dC$  and the price of Mid-Continent crude is shown in Fig. 1.<sup>1</sup> The curve for  $R$  is readily found, for  $R = dS \div dC = \text{Log } S - \text{Log } C$  and if  $S$  and  $C$  are plotted on semilog paper, the curve for  $R$  may be taken directly from the distance between these two curves from month to month.

The close relation between price and the expression  $R = dS \div dC$  would seem to indicate that at present a large or sustained change in the ratio of the rate of change of consumption and stocks is influential in bringing about price changes. As the ratio curve moves up, consumption is increasing faster than stocks increase, and as the curve moves down the rate of stocks increase is the greater. During the period *A*, there was every reason for prices to increase, but this was during the war when there was war-price regulation. At the close of this period, there was a great slump in consumption which coincided with the end of the war. During the period *B*, consumption began to increase more rapidly than stocks with the resulting rise in prices starting in November, 1919. During the period *C*, there was little change in the relative volume of consumption and stocks and no change in price. During the period *D*, which coincided with the period of general industrial depression of the country, the rate of stock increase was the greater for nine consecutive months; and after this condition had held for four and a half months prices began to drop. Prices continued to drop until they were influenced more by the actual cost of drilling than by the conditions of stocks or consumption, but an immediate recovery of consumption brought about a recovery of prices during the period *E*. During the period *F*, there was again a more rapid increase in stocks than in consumption; but during the first six months of 1922, there was a decided tendency on the part of the entire petroleum industry to attempt to stabilize prices. Also, the Mexican situation was such that relief from that quarter was momentarily expected. The price decline that the ratio curve indicated as being due in January, 1922, did not occur until July, when consumption was relatively on the increase. The rise and fall of price during the period *H* were due to an adjustment of the position of several of the larger purchasing companies in the crude market and had no connection with the general economic situation. The price change in the period *I* follows no change in the ratio curve, which would indicate some new influence. This influence is inventory rather than stocks.

### *Inventory vs. Consumption*

Enough data are not available to indicate what the exact relation is between inventory, consumption, and price. There is every evidence that the price changes during the period *I* were due to the fact that the stocks of the country, irrespective of the volume of consumption, had become

<sup>1</sup> A portion of this curve was printed in *Oil Weekly* (Jan. 20, 1923).

a financial burden that the industry was unable to bear. It is probable that when the inventories in any industry become excessive prices will fluctuate widely although there is little change in consumption. The upward tendency in prices, starting late in December, 1923, would indicate that the petroleum industry had adjusted its financial situation with respect to the financing of stocks and that prices in the near future may again be influenced by the stock-consumption change ratio. This change, as stated before, is also influenced by an anticipation that there will be a draft on stocks. The present price level cannot be maintained if there is not a draft on stocks in the near future.

### *Production, Stocks, and Inventory vs. Demand*

We have nothing on which to base any supposition as to what will happen to prices when demand cannot be met to the extent that demand rather than consumption will influence price. Prices will be governed by the economic value of the oil to the consumer. It will be a condition where the price will be influenced by the price that the consumer is willing to pay as much as by the price that the petroleum industry is willing to take.

### LAW AS APPLIED TO GASOLINE

The variables in this case are defined as before except the following:

*Production*: The output of all refineries.

*Stocks*: The volume of gasoline held by refineries.

### *Production vs. Consumption*

As in the case of crude oil, the relation production vs. consumption would only operate if the stocks of gasoline were economically very small. Curves of either production divided by consumption or the ratio of change of production and consumption show no relation to the price of gasoline. Fig. 2 shows the curve of the relation  $R = dP \div dC$ .

### *Stocks vs. Consumption*

A curve of the number of days, supply of gasoline shows no relation to price and indicates that the law is not expressed by this ratio. The relation  $R = dS + dC$  is shown in Fig. 2. An inspection of this curve shows that there is no relation between this expression and price.

### *Inventory vs. Consumption*

It is probable that the volume of stocks of gasoline has been so large for the past four years that the difficulty of providing storage has had an influence in keeping down prices. When stocks or inventories are exces-

sive, fluctuations in price may be expected to be erratic and variations in consumption would have only a minor influence on price. As soon as the relation of consumption to refinery output changes so that stocks or inventories are no longer economically excessive, the law of supply

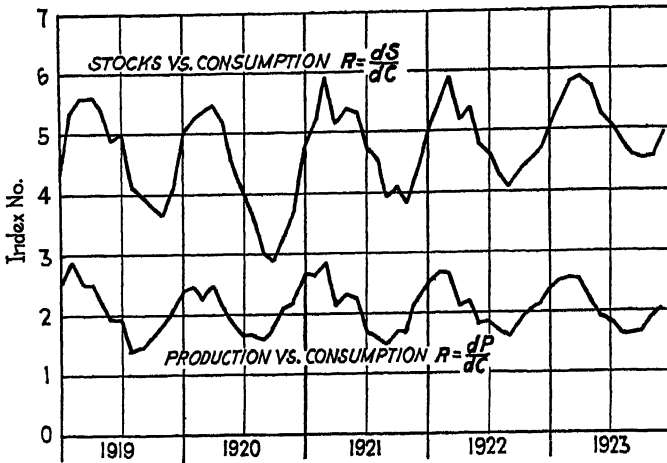


FIG. 2.

and demand will no longer operate under the inventory vs. consumption phase of the law.

The relation between gasoline prices and the volume of stocks during the past four years is shown in Fig. 3. The years 1920 and 1922 form

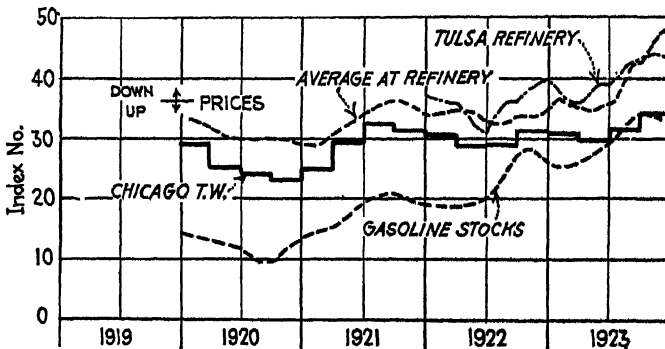


FIG. 3.—GASOLINE PRICES AND STOCKS.

a period in which it is difficult to determine whether the volume or the inventory of gasoline was the predominant influence but both had more influence on price than had consumption. During the year 1923, it seems certain that inventory had the greater influence on price. In Fig. 3, price follows the general trend of stocks with remarkable regularity.

The curve of stocks of gasoline shown in Fig. 3 is the average of three curves in which the influence of seasonal changes has been approximately eliminated. The first of these curves was obtained by considering the seasonal changes of the year 1918 as being typical. The stocks on hand for each month during the following years were plotted as a percentage of the corresponding month in the typical year. The second and third curves were procured by considering 1919 and 1920, respectively, as being typical years and plotting the curves of the following years as percentages over the type year. These three curves were averaged to give the stock curve of Fig. 3.

#### SUMMARY

The general law of supply and demand, as applied to the petroleum industry, is composed of a number of distinct laws or relations between production, stocks, consumption, etc. The law that is in control at any time depends on the conditions within the industry at that time. No one law can be applied to cover all price changes.

When conditions are such that one law holds for some time, there is a close similarity between some mathematical expression of the law and the curve of price. The author contends that the curves presented are conclusive proof that the prices of petroleum and its products are not subject to manipulation.

## Oil and Gas Leases\*

By RUSH GREENSLADE, TULSA, OKLA.

THE oil and gas lease is the basic contract of the oil and gas industry; it is the foundation stone upon which the producing industry, particularly, is based. As the industry is precarious and highly speculative, the foundation contract should be of the utmost integrity and certainty. But right there an anomaly exists; the oil and gas lease is the most obscure, most uncertain, doubtful contract in the realm of law today. That is a condition that must be considered when taking oil and gas leases, and when buying, selling, and holding them.

It may fairly be asked why should this industry rest upon so insecure a foundation. Why should not the oil industry rest upon the contract that is the basis of all industry, the warranty deed? There are many contributing reasons, but the principal one is business expediency.

The Anglo-Saxon idea of ownership of land is that every land owner owns from the center of the earth to the sky—all that is above and all that is below—consequently the oil and gas are owned by the person who owns the surface. That idea is not exactly true with reference to oil and gas, for many states have adopted the doctrine that oil and gas are like wild animals; they are fugacious and migratory and belong to the man that traps them. But, except for that doctrine, we believe that oil and gas are owned by the owner of the surface, wherein we differ from the Latin-American countries where the mineral rights are owned by the government.

The United States was settled largely by homesteading. The owners of land were, in the main, farmers, who did not have the means or the faith to drill for oil or gas. The operators or speculators did not want to buy the land on the mere possibility of finding oil; hence a compromise resulted by which the land owner gave the speculator or the operator what he called an oil and gas lease, or a right to go upon his land and drill for oil and gas. What is supposed to be the first oil lease placed on record reads as follows:

Agreed this 4th day of July, A.D. 1853, with J. D. Angier of Cherrytree township in the county of Venango Pennsylvania that he shall repair up and keep in order the old oil springs on land in said Cherrytree township, or dig and make new springs, and the expense to be deducted out of the proceeds of the oil, and the balance, if any, to be

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equally divided, the one-half to J. D. Angier and the other half to Brewer, Watson & Co. for the full term of five years from this date, if profitable.

BREWER, WATSON & Co.  
J. D. ANGIER.

Crude as that may seem, it contains the germ of present oil and gas leases, and when that form is compared with the forms in use today we will see that it is not nearly so crude as it seems at first. If an oil and gas lease is the foundation stone of the industry, is the basic contract, we should know something about what it is and the nature of the rights conferred by it.

### LEASE FORMS

An oil and gas lease is a contract by which one man, who owns a tract of land, grants to another man the right to go upon his land and take away oil and gas or other minerals. That is the heart of the contract. All else is merely incidental or is intended to conserve or modify the primary right. That primary right is what lawyers call an incorporeal hereditament, meaning thereby something that can be inherited. An incorporeal hereditament is an intangible right, a spirit right, something attached to land but not a part of the land; in other words, a profit or a right attached to land growing out of the land and capable of being inherited. Blackstone says:

Common, or right of common, appears from its very definition to be an incorporeal hereditament; being a profit which a man hath in the land of another. . . . Common of turbary is a liberty of digging turf upon another's ground. There is also a common of digging for coals, minerals, stones and the like.

This differs from common of pasture because it grants the right to take away the land itself.

A century before the first oil and gas well was drilled Blackstone and the lawyers of that day had in mind what is an oil and gas lease today; namely, what he calls a common of turbary, or the right I have to go upon your land, extract your oil and gas, and carry it away.

In Oklahoma, there are two principal forms of oil and gas leases—departmental and commercial. Departmental leases are those prescribed by the Secretary of the Interior for use upon restricted Indian lands. There are three principal forms, one each applying to the Five Civilized tribes, the Osages, and the uncivilized tribes in the western part. Those lease forms are arbitrarily fixed by the Department of the Interior and cannot be changed; they can only be procured by complying with the rules and regulations of the Department. There is no room for barter or trade except as to price; the form of the instruments themselves cannot be changed.

Aside from the restricted Indian lands, which are rather large but in proportion only a small part of the acreage in Oklahoma, there is no public land in Oklahoma or in Kansas; that is, land owned by the United States Government. There is a possible exception in certain river beds. The only public land in Oklahoma outside of certain river beds are Sections 16 and 36 in Oklahoma Territory, which have been, and may now be, school lands; that is, they have been given to the State of Oklahoma for school lands and, if not sold by the State of Oklahoma, are still school lands. Aside from these, all the land in Oklahoma and Kansas is privately owned and is subject to oil and gas leases.

A year or so ago a number of operators, coöperating with the Mid-Continent Oil & Gas Association, prepared a new form of oil and gas lease which is known as the Mid-Continent form 88; this I regard as the most up-to-date and complete form of commercial oil and gas lease in use. I am not sure that it is used very generally, but it should be.

#### RIGHT TO GO UPON THE LAND .

There are six aspects of that lease to which I want to call your attention as briefly as possible. In the first place, the grant itself, which is as follows:

That lessor, for and in consideration of the sum of \$. . . . . in hand paid, and of the covenants and agreements hereinafter contained to be performed by the lessee, has this day granted and leased and hereby grants, leases and lets unto the lessee for the purpose of mining and operating for and producing oil and gas, casinghead gas and casinghead gasoline, laying pipelines, building tanks, storing oil, building towers, stations, telephone lines and other structures thereon to produce, save, take care of and manufacture all of such substances, and for housing and boarding employees, the following described tract of land.

Here, I would call attention to the fact that although both are mixtures of hydrocarbon compounds, oil and gas are not synonymous terms. As used colloquially or legally, oil is not gas and gas is not oil, and casinghead gas is neither, although it has been claimed to be oil. Consequently, a lease for oil only is not fulfilled by drilling a gas well; and, conversely, if a lease is made to read "as long as gas is found in paying quantities," it will not be held by an oil well. In the Osage, for example, there are gas leases and there are oil leases, and they are sold separately.

Practically all of the oil and gas leases in common use are full enough in this particular, with possibly one exception—the use of the premises for building houses for employees. Considerable controversy has arisen in the last few years concerning that subject, and it is well to avoid the question by inserting in the lease a particular provision giving the lessee that right.

No matter how many tracts of land are described in the lease, it is one lease. In other words, the lease may describe five or six tracts of

land, yet the drilling of a well upon any one of those tracts or the production of oil upon any one of those tracts operates to hold the entire amount of the acreage. Each contract rests upon its own bottom; it stands or falls by itself, regardless of the fact that the land is in one tract, two tracts, or ten tracts, contiguous or non-contiguous.

#### DESCRIPTION OF LAND

Practically all the land in Oklahoma and Kansas and the other Mid-Continent states has been surveyed by the United States Survey and should be described by township, section, and range. In states where the lands are not surveyed, they must be described by metes and bounds, or by boundaries; then the question is to have the description certain and definite. I recall examining a lease on a large amount of land in New Mexico that described the land by metes and bounds. It started with a black-oak tree, followed to a point some distance away, and finally to a canyon, thence down the canyon to "the place where the men were killed." I thought that there might be some question about the place where the men were killed, but as a matter of fact that was a good description, because the point so designated was locally well known and well fixed; it was the place where a party of explorers was drowned while fording the creek in that canyon. Though it seemed indefinite and uncertain, this was actually a good description.

#### TERM OF LEASE

The next point to which I would call attention is the term of the lease, which is as follows:

This lease shall remain in force for a term of ten (10) years and as long thereafter as oil, gas, casinghead gas, casinghead gasoline, or any of them is or can be produced.

In practically all oil and gas leases there are two terms—the primary, or fixed, term and the secondary, or indefinite, term. The primary term is usually five or ten years; the secondary term, "as long thereafter as oil or gas is produced." When taking, buying, or selling a lease, the term is very important. For example, a lease broker buying a cheap lease with the thought of selling it should endeavor to obtain a long term lease because it is easy to sell. For an operator buying a piece of close-in acreage that he wishes or is willing to drill within the next year or so, the term is immaterial so long as it will give sufficient time to complete the well. For a geologist who has located a structure and is endeavoring to block that structure and sell the block, or have the block drilled, the leases should contain terms long enough to give the operator a chance to drill a test well and hold the remaining leases without having to drill



on them. These are simply matters of detail, and yet they are generally overlooked.

In that connection, it must be borne in mind that in calculating the time the first day is included and the last excluded. Consequently, a five year oil and gas lease dated March 8, 1924, will expire on March 7, 1929, and not on March 8.

### DRILLING AND RENTALS

From a practical standpoint the drilling obligation and the rentals form the most important, if not the most important, points of an oil and gas lease. Leases are classified as what are colloquially known as "unless" leases and "or" leases. An "unless" lease is, for example, a Producer's form 88 lease, which provides, in substance, that it shall terminate on a certain day or at a certain time one year from date *unless* the lessee commences a well, completes a well, or pays a rental. In other words, it creates an option on the part of the lessee to hold that lease by drilling or by paying; if he does neither the lease automatically terminates, as he is not obligated to do either.

What is called the "or" lease provides, in substance, that the lessee *agrees* to drill within a certain time *or* pay a certain rental. If he fails to pay the rental, the lease does not automatically terminate and the lessor may sue the lessee to collect the rental. In other words, he is obligated to do one or the other, drill or pay.

Again, leases may be termed "complete" leases or "commence" leases, which is a very vital distinction. I can illustrate this by the provisions of this Mid-Continent form 88. This is a lease for ten years and it must be producing within that period in order to continue longer, but the lease provides that if the lessee shall commence to drill a well within the term of the lease, or any extension thereof, the lessee shall have the right to drill such well to completion with reasonable diligence, and if oil or gas, or either of them, be found in paying quantities, the lease shall continue and be in full force and effect. In other words, if you commence a well within the term you will have the right to go ahead and complete the well and hold the lease regardless of whether it is after the term; but if that provision is not in the lease, the well must be completed and producing within the primary term.

Let me illustrate how that is important. An operator has a group or block of scattered leases. A Wilcox test well is completed; for example this well at Stroud, 4100 ft. deep, which would cost \$50,000 or \$75,000 to drill. Some of his leases in that vicinity are due to expire within three months. If he has a "complete" lease, he cannot do anything with it for he cannot complete a well on the lease within the term. If it is a "commence" lease, he may be able to await developments and see

whether he is outside or off the structure before he commences his well, being secure in the fact that if he does commence the well he may complete it.

In this same connection you have the provision about the payment of rentals. The average lease is not taken with a view to immediate drilling; most oil and gas leases are taken with the intention of holding them for a number of years, and in order to hold them the rental must be paid. The provision of this particular form is:

If operations for the drilling of a well for oil or gas are not commenced on said land on or before one year from this date, this lease shall terminate as to both parties, unless the lessee shall, on or before one year from this date, pay or tender to the lessor or for the lessor's credit in the ..... Bank at ....., or its successors, which bank and its successors are the lessor's agent and shall continue as the depository of any and all sums payable under this lease, regardless of changes of ownership in said land or in the oil and gas, or in the rentals to accrue thereunder, the sum of ..... Dollars which shall operate as rental and cover the privilege of deferring the commencement of drilling operations for a period of one year.

In other words, within one year the lessee must pay the lessor a certain rental, or pay it to the bank for his credit. That provision is further modified or enlarged so that the lessee may mail a check, in order that the mailing of a check will have the effect of making the tender. That is important also. A person has no idea, unless he is familiar with the details of the business in this respect, how many contingencies arise in paying rentals. If the lessor dies, becomes insane, or moves away; to whom shall the rental be paid? The bank fails or is merged with another bank, to whom shall the rental be paid? The lease provides that it shall be paid to the lessor or deposited to his credit in the bank. When a check is mailed to the bank, is it deposited to the credit of the lessor? It is important to know that the rental is paid in accordance with the terms of the lease, and right there is the importance of the kind of a lease—if it is an “unless” lease, it automatically terminates unless the rental is paid, and paid in accordance with the lease; if it is an “or” lease, the lessee has another chance.

### PAYMENT OF ROYALTIES

Practically all oil and gas leases since the beginning have provided for a royalty. The first lease on record provided that, after the payment of the expenses, the balance of the proceeds should be divided equally between the land owner and the lessee; the custom of paying operating expenses and then dividing the proceeds is no longer in force. The Mid-Continent form 88 provides:

The lessee shall deliver to the credit of the lessor as royalty, free of cost, in the pipeline to which lessee may connect its wells the equal one-eighth part of all oil produced and saved from the leased premises.

It also provides that he shall pay so much for royalties for a gas well and one-eighth of the casinghead gas.

Theoretically, the ideal oil and gas lease should provide for a sliding scale of royalties. True conservation is supported by the sliding scale, which mitigates the royalty as the production of the well decreases. In other words, there may come a time in the production of wells in which a one-eighth or a one-sixth royalty, such as obtains in the Osage, or one-fifth in certain cases, would force the operator to shut down the wells rather than pay the royalty. However ideal that may be, such is not the custom. One-eighth royalty, by force of experience and custom, has become the accepted standard and whenever a lease is submitted with a higher royalty, especially such a royalty as one-fifth, one-fourth, or one-third, in the majority of cases, it is economically unsound and should be avoided.

It is only within the last few years that it has become important to provide for the payment of royalties on casinghead gas. The leases in the old Glenn Pool, made in 1905 to 1910, generally contained no provision for payment of royalty on casinghead gas and litigation, trouble, and loss have resulted. Practically all modern leases provide for the payment of a royalty on gas from an oil well. Personally, I have no doubt but that this means the casinghead gas, and was intended to be casinghead gas, but it is far better to remove any doubt and say "casinghead gas, where used for the manufacture of gasoline, shall pay a certain royalty." There is no need of taking any chance on the question of what is casinghead gas, whether oil or gas, or a hybrid, and there is no need of taking any chance on the question of what is gas from an oil well.

In all of these questions, the primary object to be kept in mind is to protect and circumscribe the primary right, so that the lease can be profitably operated after it has been obtained; in other words, a lease is taken to be worked, not simply to be sold.

#### RELATIONS BETWEEN LESSEE AND LESSOR AFTER DISCOVERY OF OIL

Last of all, attention is called to those features of the lease that provide for the relations between the lessor and the lessee after the discovery of oil and the property is being operated. Notwithstanding the usual provisions of the lease, the courts say that there are certain implied provisions, generally two: First, that you shall offset all producing wells on adjoining leases; second, that you shall drill and develop the lease with reasonable diligence, bearing in mind that neither the operator nor the land owner can arbitrarily control the amount of development, but they must confer with each other and agree upon a measure of development such as a reasonable, prudent business man would prescribe.

In addition to the relations in that respect, one feature that has become very important in recent years is the division of acreage. All

leases generally prescribe that when a part of a lease is assigned, the assignee may pay a rental upon his part and thus preserve his part of the lease without paying the rental upon all. It has become the custom within the last few years to speculate in oil royalties. I think what is commonly called the unit system started in the El Dorado field in Kansas. On one lease in that field the royalty was sold and divided and subdivided until the units were one-twelve-thousandth of one-eighth. Several deeds call for an undivided one-twelve-thousandth of one-eighth royalty, or a one-twelve-thousandth of the royalty on a certain 160 acres of land. In one case, the abstract of title contained about four thousand instruments and cost I do not know how much.

In addition to selling royalties in that way, it has become the custom to segregate certain tracts of land and sell 1 acre or 5 acres; what is called a 5-acre interest out of 160 acres, which is something that is unknown to the law or anything else. In addition, 10-acre tracts are carved out of 160-acre tracts, and the question arises in all those cases how the operator shall work his lease, pay his royalties, and preserve his property. In the first place, how shall he work his lease? How shall he drill his wells?

It is well settled now that the division of the land into separate tracts does not create inside lines, so that if four 40-acre tracts are carved out of 160 acres, he does not have to offset the wells on each 40 acres. All the production may be on one 40 acres and all the tanks on another 40 acres, and no production on it, but the lease will be in force.

Again, how shall the royalty be paid? The lease provides for one-eighth of the oil delivered in the pipelines. If the lease is divided into 10-acre tracts, the law says that the owner of each tract is entitled to the royalty from the well on that tract, but all the oil from all of the wells is run together into one battery of tanks. Is it necessary for the lessee to separate the tanks or set a battery of tanks on every 10-acre tract, or every 5-acre tract, in order to measure the royalty for the benefit of these separate owners? Probably it is, because the lease says that he shall deliver to the lessor one-eighth of the oil in the pipelines, and he cannot deliver that oil unless he sets a tank to measure that oil, yet that may be prohibitive in expense.

In order to take care of situations of that kind the more modern form of lease contains a special provision, which should always be inserted, to this effect:

If the leased premises shall hereafter be owned in severalty or in separate tracts, the premises, nevertheless, shall be developed and operated as one lease and all royalties accruing hereunder shall be treated as an entirety and shall be divided among and paid to such separate owners in the proportion that the acreage owned by each such separate owner bears to the entire leased acreage. There shall be no obligation on the part of the lessee to offset wells on separate tracts into which the land covered by this

lease may be hereafter divided by sale, devise, or otherwise, or to furnish separate measuring or receiving tanks.

And it is also provided that the lessee shall not be bound by any change of ownership unless and until notified thereof in writing. That simply means that if a lease originally covers 160 acres and is later sold and subdivided into four 40-acre tracts, the owner of each 40-acre tract will not receive a royalty of one-eighth of the oil on that 40 acres, but one-fourth of one-eighth of the royalty on the entire 160 acres. All questions of inside lines are removed, all questions of the measurement of the oil are removed, and the operator may operate the lease as one indivisible tract and pay to the land owners in proportion as the acreage of each bears to the entire fee.

I wish I could say that that provision is sound and will be sustained, but it is in the courts of Oklahoma today and the outcome I cannot foretell. Theoretically, it is a legally sound, fair provision for both the lessee and the lessor, but whether or not it will be ultimately sustained cannot be told at this time.

#### OBTAINING LEASES

As to the method of obtaining leases and as to the procedure to be gone through in procuring the title, etc., it is sufficient to say that an oil and gas lease is like a deed; it conveys an interest in land, and it must be signed, acknowledged, and recorded like a deed. It does not have to be signed by the lessee. Like a deed, when it is accepted it is yours. It should be examined by a reputable lawyer before it is paid for, and an abstract of title should be taken and preserved. All of these questions are questions of detail of acquisition, but nevertheless important.

If the men engaged in the business of leasing, the reputable lease buyers and lease brokers as well as the engineers and geologists, who are occasionally the primary buyers and sellers of leases, would study the prevailing lease forms, familiarize themselves with the more important provisions of the leases, much trouble would be averted, and many questions that later confront the operators would be avoided.

#### DISCUSSION

MR. GREEN.—Producers' form 88 is generally considered a "commence" lease, is it not?

MR. GREENSLADE.—A "complete" lease ordinarily.

MR. GREEN.—If a well is started before the term has expired, or within the 5 years, does not the lessee have the privilege of completing the well?

MR. GREENSLADE.—He does not. Producers' form 88 says: "If no well be commenced on said land on or before the .. day of .....this

lease shall terminate as to both parties, unless the lessee shall on or before that date," etc. pay a rental; but that lease is for a definite term. It does not contain the provision that allows the lessee to complete the well after the expiration. Consequently, unless he has production within the 5 years, or the 10 years, the lease is automatically ended. It must have a special provision giving him the right to complete the well he has started within the term.

MR. CORDELL.—In the strictest sense, what is commencing a well?

MR. GREENSLADE.—"Commence operations" is an indefinite term that has been held to mean anything from building a road to laying a water line. I do not like the phrase, and would avoid it if possible; but to "commence operations for a well," which is a phrase sometimes used, will include any work that legitimately tends toward the drilling of a well, such as laying a water line, in some cases building a road, if necessary to haul in the rig timbers. "Commence a well" means to commence operations for a well. "Commence drilling a well," I take it, means actual spudding in. I do not want to be too dogmatic about those things, but that is my understanding.

MR. CORDELL.—Is it legal, where a block of leases has been secured on contiguous properties, to insert a clause providing that if a well is started on any one it will hold all the others, provided all the others are agreeable to it?

MR. GREENSLADE.—Yes, that is legal, if it is carefully and definitely so provided. Frequently blocks of acreage are taken with the understanding that a well shall be drilled or commenced within a certain time within  $\frac{1}{4}$  mile of a certain point.

MR. PAW.—If that is the case, why is it not legal for the lessor and the lessee to agree definitely as to how the oil lease should be handled? In other words, if it is sold in parcels, it shows right then it was contemplated that a burden might be put on the operator which would make it more expensive to operate that lease than his profits would justify. Why cannot the parties agree to that, and why is not any subsequent buyer bound by that?

MR. GREENSLADE.—I know of no possible reason why that is not perfectly binding on not only the parties to the lease but subsequent buyers. In the litigation that involves that question at this time there is only one reason I have heard advanced why that provision was not good. In that particular case, a lease covered 160 acres of land. The first royalty sold there was an undivided one-half interest in a 40-acre tract, which happened to be the southwest 40 acres of that 160. When it came time to pay the royalty, the purchaser of the half interest in that 40-acre tract demanded one-half of one-eighth of the royalty in the wells on that 40-acre tract. When his attention was called to the provision in the lease, which said that he could have but one-eighth of the royalty

on the whole, he said, "Why, that was the nearest 40-acre tract to production, and I paid more for that tract because it was nearest to production when I bought it, and consequently it is mine."

MR. PEW.—But he bought it with the definite provision before him that that lease was to be operated as a whole?

MR. GREENSLADE.—Exactly; but it so happened that he had not read the lease.

MR. PEW.—That was not the lessees' fault.

MR. GREENSLADE.—Well, that man seemed to think it was.

MR. PEW.—What recourse has a lessee if he has an "88 form" lease and the bank fails and he cannot locate the lessor?

MR. GREENSLADE.—He is out of luck if the bank fails without any successor. Most leases provide for deposit in a certain bank or its successors, and they should so provide. Consequently if the bank fails, or it is taken over by another or the two are merged, the money would be paid to the successor bank. But in the case of an "88 form" lease, if the bank should fail and the lessee could not locate the lessor to make a payment to him, I know of no way he could preserve the lease. It might be it could be done, but as the lease provides that he must pay and he has not paid, I do not know how he is going to help himself.

MR. PEW.—Is it the lessee's fault that the bank failed? Does not the lessor name the depository, and is not he responsible for that?

MR. GREENSLADE.—Yes; but the bank is the agent of both the lessor and the lessee, and the latter agreed when he took the lease that he would pay the lessor or deposit it in the bank. Now, if he does not do either, regardless of whose fault it is, how is he going to keep the lease?

MR. PEW.—The money could be mailed to the last known address.

MR. GREENSLADE.—That is the big fault, in my judgment, of Producers' form 88. That lease, although probably the most widely used in the Mid-Continent field, is absolutely the worst, because it is a lease that may automatically terminate through no fault of the lessee.

MR. PEW.—But it would be a fault on the part of the lessor. It is his business to keep himself in sight. He could hide and defeat the purpose of the lease.

MR. GREENSLADE.—Absolutely; and that is the particular fault in that form of lease.

MR. WHITE.—If one lease includes several tracts of land that are not contiguous will the royalty be handled as though it were a single piece of land?

MR. GREENSLADE.—Yes, if it contains the provision to which I have referred; if it does not contain that special provision, the owner of each particular tract on which a well is located will obtain the royalty on that well.

MR. WHITE.—If one man owned three or four quarter sections and leased them under that new form and later sold the royalty on one quarter section, if there is production on another section would the buyer come in on that production?

MR. GREENSLADE.—He would if the lease provided that it shall be operated as an entirety, and each lease holder shall share in the royalty; otherwise he would not. Production on 10 acres might hold the lease.

MR. SCHUERMEYER.—Inasmuch as the Courts of equity have given their aid to preventing default where, for instance, the mails have failed to carry rental in time, where there is a failure of a bank, or a failure of some fact for which the lessee is not responsible, suit could be filed and a tender of the money made to the Court, setting forth the facts and setting forth the ability and the readiness to perform all of the conditions of the lease, do you not think the Courts would lend aid to prevent a default of that lease?

MR. GREENSLADE.—They could do so.

MR. SCHUERMEYER.—The Courts have not taken the view that Mr. Pew has indicated about the harshness of that rule with reference to the payment of all of the royalties to the one holder. They took that position because the counsel for all of the oil companies filed a brief insisting that that should be the rule; it was a close question before the Court at that time, and the Court was divided on that subject. A lot of those questions have been close questions; with the new questions being put up, the Courts will lean to the oil operator as readily as to the owner.

MR. GREENSLADE.—I agree with you that the Court should relieve most unfortunate mistakes of that kind. The Federal Courts do and have, in the past, relieved against forfeitures on account of mistakes of that character, not only on the "or" leases but on "unless" leases, Producers' 88 leases. The State Court has not been so lenient.

MR. KATES.—If the new Mid-Continent form were more fully understood that form might be used more than it is now.

MR. GREENSLADE.—That is true, it is a process of education. The provisions of Mid-Continent 88 about the payment of rentals are as follows:

If operations for the drilling of a well for oil or gas are not commenced on said land on or before one year from this date, this lease shall terminate as to both parties, unless the lessee shall, on or before one year from this date, pay or tender to the lessor or for the lessor's credit in the ..... Bank at....., or its successors, which bank and its successors are the lessor's agent and shall continue as the depository of any and all sums payable under this lease, regardless of changes of ownership in said land or in the oil and gas, or in the rentals to accrue thereunder, the sum of ..... Dollars which shall operate as rental and cover the privilege of deferring the commencement of drilling operations for a period of one year. In like manner and upon like payments or tenders, the commencement of drilling operations may be further deferred for like periods successively. All payments or tenders



may be made by check or draft of lessee or any assignee thereof, mailed or delivered on or before the rental paying date.

In other words the attempt has been made there to relieve the lessee of all of the mishaps in the United States mails or the Oklahoma banks.

The provision about royalty is like most all others, but it contains the provision for notifying the lessor of changes of ownership and the furnishing of certified copies of transfer or assignment, etc. It says:

If the leased premises shall hereafter be owned in severalty or in separate tracts, the premises, nevertheless, shall be developed and operated as one lease and all royalties accruing hereunder shall be treated as an entirety and shall be divided among and paid to such separate owners in the proportion that the acreage owned by each such separate owner bears to the entire leased acreage.

The Department of the Interior is now engaged in preparing for promulgation a new form for departmental lease. A special committee of the Mid-Continent Oil & Gas Association is conferring with the Department in an effort to mitigate somewhat the harshness of the present departmental forms. One of the things the committee is insisting on is the inclusion of that provision in the departmental form of lease.

MR. CORDELL.—Can a person get up his own form of contract and have it printed—contract for leases?

MR. GREENSLADE.—Yes.

MR. CORDELL.—Could he, in any manner, alter the provision for one-eighth of the oil or gas?

MR. GREENSLADE.—Yes; it is a matter of contract between the parties. The custom of one-eighth is the result of years of experience. It can be 50 or 100 per cent.

MR. FEW.—Two objections might be made to the Mid-Continent 88 form. One is that the lease provides, substantially, that the royalty shall be paid to the owners in proportion to their ownership; that might be \$1 or \$10 or \$10,000. Should not a clause be added providing that if the division of this ownership becomes a burden the owners of the royalty shall provide the additional expense and that this shall be a charge against them? The other objection is, no provision in that lease permits the owner, and the law would not permit him, to hold adverse title to his lessor to care for any tax defaults.

MR. GREENSLADE.—Yes; there is a provision in there about that, but I did not read it.

With reference to the other objection, I think it would be beneficial to provide in a form of lease that in case the ownership becomes so numerous, for example, the owners should appoint a trustee to hold the royalties. That has been done in many cases and operators have arbitrarily insisted on its being done. That point was considered by the

committee at the time they prepared that form of lease, but after some discussion it decided not to put that provision in the lease.

MR. NIXON.—I wish you would read the provision with reference to rental and the royalty in the division of the land.

MR. GREENSLADE.

If the leased premises shall hereafter be owned in severalty or in separate tracts, the premises, nevertheless, shall be developed and operated as one lease and all royalties accruing hereunder shall be treated as an entirety and shall be divided among and paid to such separate owners in the proportion that the acreage owned by each such separate owner bears to the entire leased acreage.

MR. NIXON.—There are few land owners who would understand what that means, and an explanation would cause you to lose the lease. But an unfair advantage would be taken of the man, to have him sign a lease in that form without an explanation. Where a man owns several diversified tracts, he might later sell one not knowing that when he was selling that tract he was also bartering away a portion of the oil under a tract that might be miles away from it.

MR. GREENSLADE.—I do not agree with you; the land owner is in duty bound to read his contract as much as a lawyer. However, there is some food for thought in that suggestion. It is a matter that should be explained to the land owner when the lease is taken. When explained I do not believe it will result in difficulty for this reason—it does not prevent a sale in any way. It may result in one man purchasing a royalty when he has no wells on the tract that he bought, but generally speaking those things will even up in the long run and if the clause is properly explained no difficulty will arise in getting the lease. Oil and gas leases should be fully explained to the lessor. The courts generally consider them like life insurance policies, for example. In other words, they are construed more favorably for the lessor, or the land owner, in cases of doubt for two reasons. In the first place, because it has been thought that such construction would hasten development, which is the object of the lease. In the second place, it has been thought that oil and gas leases, like an insurance policy or something of that character, contain a great deal of technical language, presumably not known and not generally understood by the public at large, so in cases of doubt the courts lean toward the land owner in construing them. For that reason care should be taken to explain all doubtful provisions of the lease.

MR. NIXON.—Where the unit system is used and innumerable assignments are made on some one tract, I think you are absolutely right. But if a man owns 160 acres in sections 3, 5, and 7, and later sells the one in section 5, and if section 3 would produce and sections 5 and 7 would not, it is an unfair advantage to have the purchaser of the tracts of 5 and 7 share in the royalty in 3.

MR. GREENSLADE.—That works both ways. For example, the tract that was sold might produce and the one that was kept might not, and you would share in the other royalty.

MR. CORCORAN.—You said that Producers' form 88 provided that the failure of the bank or losing of the lessor's address forfeited the lease, I do not see that has been corrected in Mid-Continent form 88.

MR. GREENSLADE.—My statement was that this form does not obligate the lessee to do anything; it is a mere option. He does not have to drill; he does not have to pay any rental, but unless he does one of the two his lease automatically terminates. As a result, a failure to pay a rental may result in his losing the lease, because it automatically terminates unless he does pay.

In the Mid-Continent form 88, an attempt was made to do away with contingencies that may result in such forfeitures by putting a duty upon the lessee that, if he fulfills, will keep his lease alive, namely, the duty of paying by mailing a check. In other words, his right to keep that lease is not made contingent on other people but on his performing a certain duty, namely, mailing a check.

MR. HUTCHINSON.—The chief objection to the Mid-Continent form is that a ten-year period is printed in the lease. If that lease provided for both five and ten years, as the owner is more accustomed to a five-year lease than to a ten-year, there would be little difficulty in getting it executed.

MR. GREENSLADE.—There are two sides to that question. It is probably true that the land owner usually thinks of a five-year lease and that is the easiest to get. If you print a lease with blank years or with five years in it, you are to get a five-year lease. If the printed lease provides for ten years, you will get some ten-year leases because it takes some work to change that ten to five.

MR. KATES.—The five-year period has become almost as customary as the one-eighth royalty. If this lease is going to be widely circulated, at least some should be printed with five years, and the broker should go out with both in his pocket.

MR. GREENSLADE.—There is some merit in that suggestion. Generally, however, wildcat leases are being taken for ten years instead of five.

MR. LOVEJOY.—Our company has been successful in the last few months in taking 200 or 300 leases on that form. Our lease men compare this form with the old lease. The old lease is ambiguous and does not tell the landowner what he is going to get, while the new lease tells him absolutely what he will get.

MR. SMITH.—Can an owner sell all of his royalty without selling his surface rights?

MR. GREENSLADE.—He can.

MR. UMPLEBY.—I fail to comprehend how the mailing of a notice or a check that is not received by anybody is going to be proven from the standpoint of the lessee.

MR. GREENSLADE.—Of course, the mailing of a check that is not received would not constitute payment; what it does do is fulfill the condition of the lease.

MR. UMPLEBY.—How could you prove that you have done that?

MR. GREENSLADE.—If it is sent by registered mail, you would show that fact by the registry receipt.

MR. UMPLEBY.—That does not show the contents.

MR. GREENSLADE.—Oh, no; you would have to prove that the same as you would prove any fact, by witnesses, of course.

MR. UMPLEBY.—That is within your own organization?

MR. GREENSLADE.—Absolutely. The mere mailing of a check that is not received does not constitute payment. If the check is lost in the mails, the lessor may insist on the issuing of a duplicate check to pay the rent. What it does do is to fulfill the contingency, which keeps the lease in force.

MR. UMPLEBY. It simply gives you time.

MR. GREENSLADE.—It may require you to issue a duplicate check or you may have to pay it twice, but you do not automatically forfeit your lease rights.

MR. DAY.—I would like to make one suggestion to the committee that is conferring with the Department of the Interior on the new form of departmental leases. Where a particular tract of land is assigned out of a lease—say, for instance, a lease covering 160 acres and you assign a particular tract, 40 or 80 acres, the Department holds that where all of that tract is being assigned it is considered two leases, which is not done under the commercial lease. That is unjust, and if we are going to reorganize this departmental lease that clause should be taken care of.

MR. GREENSLADE.—That is taken care of in the amendments which the committee of the Mid-Continent Oil & Gas Association has suggested to the Department.

MR. DAY.—There is nothing in the rules and regulations that give the Department the right to do that; it is assuming that right.

MR. GREENSLADE.—I know it has assumed that right, and I do not think it has been admitted by a lessee who has been affected by it.

MR. NIXON.—An early United States Supreme Court decision holds that the assignment of a lease does not constitute another lease.

MR. HUTCHINSON.—When paying royalties, do you recognize the royalty holders who have not served written notice as provided? Are they entitled to the royalty?

MR. GREENSLADE.—They are if you know them.

MR. HUTCHINSON.—Suppose they have not served any written notice?

MR. GREENSLADE.—Do it anyway. I have always felt that it was unwise for a lessee to rely on provisions of that kind in a lease when he had actual knowledge that the transfer or change in ownership had been made. The purpose of that provision in the lease is to apprise the lessee. If, however, he does have actual knowledge of the change of ownership from some other source, he should take cognizance of it.

MR. HUTCHINSON.—Suppose you fail to take cognizance of it; it is in the lease that they have to serve written notice.

MR. GREENSLADE.—If you fail to, you can rely on your lease.

## Electric Welding of Large Storage Tanks

By HAROLD C. PRICE, E. M., BARTLESVILLE, OKLA.

(New York Meeting, February, 1924)

ONE year ago, that is in January, 1923, there had not been constructed a single oil-storage tank of 55,000-bbl. or more capacity with a completely electric welded roof and bottom. Today, there are at least fifty 80,000-bbl. storage tanks completed, or nearing completion, on which both the roofs and the bottoms are electric welded. It is the purpose of this paper to describe, in a general way, the construction of these

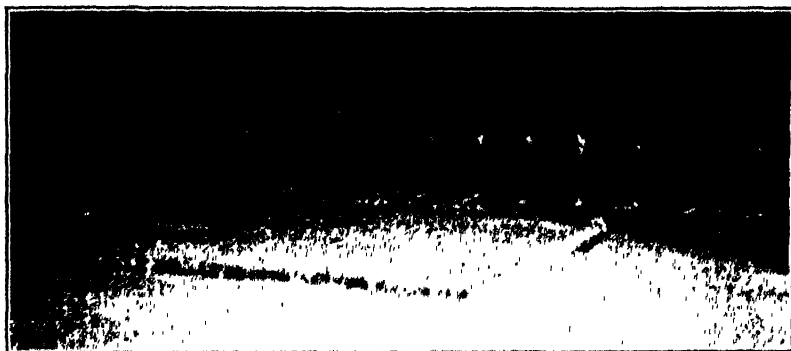


FIG. 1.—ELECTRIC-WELDED SEAMS AND RIVETS OF BOTTOM IN 55,000-BBL. TANK AT EL DORADO, KANS., SHOWING ALSO PATCH PLATE WELDED TO BOTTOM.

welded roofs and bottoms, and to give their advantages over riveted construction. All of the following data and conclusions were obtained from observations made during the welding of tanks by the Welding Engineering Co. at Texas City, Tex., and Tonkawa and Burbank, Okla.

As far as can be determined, the first electric welding on large tankage was completed in May, 1922. At that time the Empire Companies of Bartlesville, Okla., discovered a badly leaking bottom in a 55,000-bbl. tank at El Dorado, Kans. They had considered concreting this bottom, but because of the much smaller cost, decided to try electric welding; so a contract was given the Welding Engineering Co. of Bartlesville, Okla. In this instance, no new sheets were added, the bottom being repaired by electric welding of all seams and rivets, Fig. 1. In some places where the original rivets were missing, the holes were filled by welding; patch plates were also added at certain badly worn spots. This tank has since been used for over a year and a half, but no other

leaks have been discovered. The cost of electric welding was about one-half that of a concrete bottom.

Shortly after this, the Cosden Co. began to electric weld the roof seams on the storage tanks at its refinery at Tulsa. These, however, were riveted roofs, the rivets being laid at a pitch of 4 in. The welding, therefore, on these roofs simply took the place of the calking edge, and was not applied for strength. According to the officers of the company, welding has furnished a gas-tight roof.

The Standard Oil Co. did some similar work at Neodesha, Kans., during this period. In the latter part of 1922, one of the large tank-construction companies erected the first all welded roof at Humbolt, Kans., but the real construction of both roofs and bottoms did not begin until February, 1923. At that time, the Marland Refining Co. let a contract to the Welding Engineering Co. to repair three 55,000-bbl. tanks at Texas City, Tex. All the seams and rivets in the bottoms of these tanks were to be welded, as were all the seams in the shell. The tanks to be repaired were hardly a year old, two of them had never been filled with oil, yet the rivets and seams were leaking badly. With the expense of these repairs in mind, the Marland Refining Co. decided that it would save considerable money if the bottoms and roofs of all tanks were welded during the original construction; therefore, contracts were awarded for nearly 50 tanks at Texas City, Tex., Ponca City, Tonkawa and Burbank, Okla., with electric welded roofs and bottoms.

### ERECTION

As there are no holes to be punched in the plates, the sheets for this work, with the exception of the sketch plates, are shipped direct from the mill to the job, without going through the shops. In most cases the sketch plates are cut in the shop; sometimes they are cut in the field by the use of an acetylene torch. The first method is the better and cheaper, for when the sketch plates are cut in the field there is considerable waste of material; also unless the film of oxide left by the acetylene is thoroughly removed from the plate there is likely to be considerable leakage through the weld. After the grade for the tank is made, the bottom sheets are laid directly upon it; no horses or scaffolding are necessary, as when the bottoms are riveted. All plates, both roof and bottom, are laid with a 1-in. lap. The bottom plates are first laid in position and tack-welded, after which the angle iron is placed in position, tack-welded, and then completely welded to the bottom, Fig. 2. After the angle iron has been completely welded to the bottom, the shell of the tank is raised and riveted, while the welding of the bottom sheets is being completed. The shell of the tank is riveted and the structural steel for the roof is erected in the usual manner, Fig. 3.



FIG. 2. WELDING ANGLE IRON TO BOTTOM.



FIG. 3.—FINISHING WELDING ON BOTTOM AS SHELL IS BEING COMPLETED.



FIG. 4.—TACKING FIRST COURSE OF ROOF.



FIG. 5.—TACK-WELDING FIRST PLATE TO ANGLE IRON ON 55,000-BBL. STORAGE TANK FOR MARLAND REFINING CO., AT TEXAS CITY, TEX.



The roof plates are then raised, by the means of a cam or screw clamp, and laid, in the usual manner, from the edge toward the center. They are tacked to the top angle and to each other as they are laid, Figs. 4 and 5. The first method was to tack the plates on the ends and in the center, in order to expedite the laying; a second welder would then permanently tack with a 12-in. spacing, Fig. 6. But by this method, because of buckling between the temporary tacks, it was often necessary to use weights or leverage to bring the plates in contact with each other. Later, two welders tacked simultaneously on each plate, working in one direction only; this eliminated the buckles and the necessity of further tacking. After the plates were tacked, other



FIG. 6.—ROOF PLATES TACK-WELDED READY FOR FINAL WELDING.

welders laid the permanent weld. On the bottoms, a weld the full thickness of the plates was used; but on the roofs a weld of  $\frac{1}{16}$  in. less than the thickness of the plates is sufficient; in other words, on  $\frac{3}{16}$ -in. plates a  $\frac{1}{8}$ -in. weld is sufficient.

#### TESTS

A rigid inspection is given all work at the end of each day; anything looking like a pinhole is marked and rewelded. The bottoms are tested by pumping oil under the tank through fourteen flanges welded onto the bottom. On the second bottom welded at Texas City, only two pinholes developed, despite the fact the bottom had been laid in very wet weather under the most difficult conditions; on the third bottom, only five pinholes developed.

The results on the first bottom showed well what not to do. In this case oil was run on the grade inside of the curbing before the plates were laid. Sloping horses, as shown in Fig. 7, were then placed across the

center of the grade, and the plates dragged upon them, the intention being to weld two courses of sheets, drag the horses out part way, lay two more courses, weld those, and repeat the operation. Two difficulties presented themselves: First, it seemed impossible to lay the sheets without getting them fairly covered with oil; this, of course, made good welding quite difficult. Then, after the horses had been pulled out and the sheets rested on the oil, the hot sun would tend to buckle the plates considerably; in addition, there was always the danger of fire, in fact one small fire did occur. Nevertheless, this bottom was finished by this method. It showed a great many buckles and developed about 100 pinholes; these were re-welded and when the tank was finally completed and tested, it showed no leaks.



FIG. 7.--BOTTOM LAID ON A CRUDE-OIL FOUNDATION, USING SLOPING HORSES.

The tests made by the Marland Refining Co. on the roofs at Tonkawa showed excellent results. Strips cut from the roofs through the weld transversely to the welded seam had an average tensile strength of 40,000 lb. per sq. in.; in other words, the weld was  $72\frac{1}{2}$  per cent. the strength of the plate, using 55,000 lb. as the tensile strength of the plate. As the strength of the joint of a single riveted roof, using  $\frac{3}{16}$ -in. plates and  $\frac{7}{16}$ -in. rivets, is only 40.1 per cent. efficient, the fear of weakness in a welded roof is completely dispelled. A photomicrograph of the cross-section of one of these test pieces is shown in Fig. 8.

Three bottoms and sixteen roofs were electric-welded during 1923, under the observation of the writer, Fig. 9. All of these tanks have been subjected to extreme changes in temperature, and to date there has not been a single evidence of failure. No cracks have developed and, consequently, no leaks. We do not mean that there have been no pinholes; there have been a few, and these were easily rewelded

or calked. The welding of these tanks was done in the worst kind of weather. The heavy rains in Texas and Oklahoma have given the practicability of the work a test not contemplated when the work was



FIG. 8.—CROSS-SECTION OF WELDED-ROOF JOINT, SHOWING PENETRATION OF WELDING METAL INTO ROOF PLATE.

started. Good welding cannot be performed on a wet surface; rains therefore delayed the work. At times, also, in Texas the dew was so heavy at night that work had to cease until the sun came up. Strong

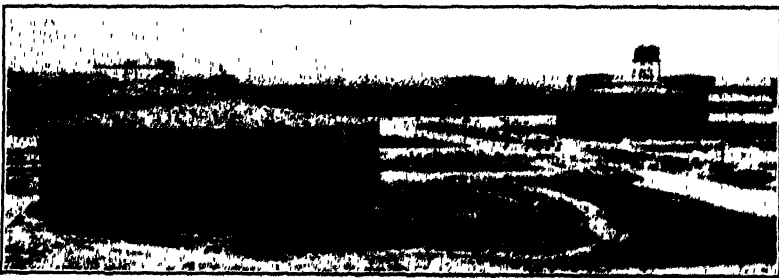


FIG. 9.—NEW ELECTRIC-WELDED ROOFS ON OLD 55's AT TEXAS CITY, TEX.

winds also caused trouble. One obstacle for which we were not prepared was the attraction of bugs to the arc. Fortunately this would occur only on very warm breezeless nights, but when it did the speed of welding was greatly reduced or welding ceased altogether, for the multitude

of dead insects not only obstructed the weld, but proved very disagreeable to the welder.

### DATA

Records kept of all welding operations on the nineteen roofs and bottoms disclose the following average welding speeds: Roofs, 16 ft. per hr.; bottoms, 14 ft. per hr.; bottom angle to bottom plates,  $4\frac{1}{2}$  ft. per hr.; tacking 70 hr. per roof or bottom.

Roof and bottom plates were of  $\frac{3}{16}$ -in. steel, except the bottom sketch plates, which were  $\frac{1}{4}$  in. Bottom angles were  $\frac{5}{8}$  in. thick and were welded to a height of at least  $\frac{3}{8}$  in. As stated, these figures are averages of all the welders; some men worked faster than others. At times under perfect conditions, speeds of 20, 25, and even 30 ft. per hr. were made. On an 80,000-bbl. tank, there are approximately 2900 ft. of roof seam, provided 6 by 18 ft. plates are used; this size plate is readily handled. Should a smaller sheet be used there would be more footage, and the cost of the welded roof or bottom would naturally increase.

### MACHINERY AND ACCESSORIES

Both electric-driven and gasoline-driven welding machines of the direct-current type, with short arc characteristics were used on this work. On the gasoline-driven machine, two shifts were used, working 18 to 20 hr. a day. On the electric-driven machines, three shifts were used, working  $22\frac{1}{2}$  hr. a day. On one of the jobs, excellent evidence was furnished as to the comparative efficiency of direct-current and alternating-current welders on this kind of work. Two direct-current and two alternating-current machines of the transformer type were working on the same tank farm, performing exactly the same kind of work, under the same kind of conditions. During two months, the cost of power for the alternating-current machines was twice as much as that for the direct-current machines, despite the fact that the direct-current machines did 50 per cent more work. The direct-current machines used 4150 kw. for welding approximately 14,700 ft. while the alternating-current machines used 9948 kw. for welding 10,000 ft. We also found the short arc of great advantage in assuring high-grade welding. It was necessary, of course, to use only the best welders. Many men who applied for work had been using long-arc machines. Some of these, the poorer welders, were unable to operate with a short-arc even after being given considerable time to practice; the better welders, however, found no trouble in operating with the short arc after working 2 or 3 hr. Because of this we were never in fear of having poor welders on the job.

Several kinds of welding rods were tried, but we found that a coated rod of  $\frac{5}{32}$  in. diameter gave the best and most uniform results and warranted the small additional expense.

## ADVANTAGES OF ELECTRIC-WELDED TANKS

The advantages of the electric-welded roof and bottom are:

1. As no holes must be punched, the plates can be shipped direct from the mill to the job without going through the shop for fabrication.
2. The bottom can be welded directly on the grade, thus eliminating the expense and time of placing the plates upon horses; the usual work-

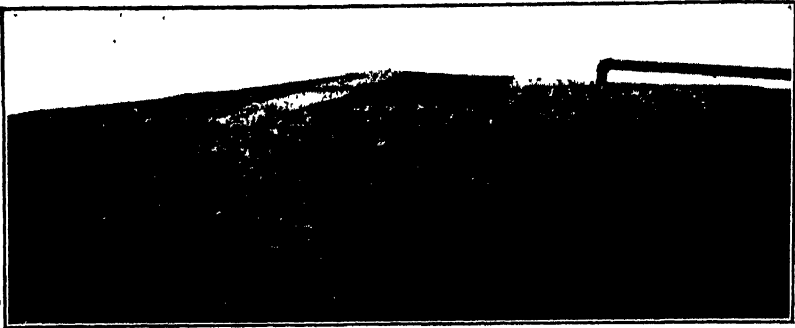


FIG. 10.—RIVETED ROOF.

ing of the rivets and calking edges in the bottom, as it is being lowered, is also eliminated.

3. Sheets are much more readily fitted in place as there are no rivet holes to be matched.

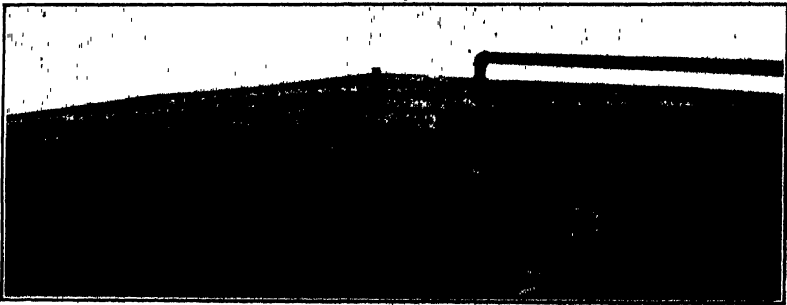


FIG. 11.—WELDED ROOF ADJACENT TO ROOF SHOWN IN FIG. 10; BOTH PHOTOGRAPHS WERE TAKEN THE SAME DAY AT SAME TIME FROM SAME LOCATION ON EACH TANK.

4. The shell can be raised while the bottom is being welded, saving time in construction.

5. The one-piece roof expands and contracts uniformly with the change of the temperature, thus working of the rivets and calking edge as on a riveted roof is eliminated. This makes the roof absolutely gas-tight and greatly reduces the fire hazard; the cost of insurance should be correspondingly reduced.

6. The roof and bottom are smoother than by riveted construction, eliminating strains caused by buckling, Figs. 10, 11, and 12.

7. A welded joint should have longer life than a riveted joint; in nearly all worn-out bottoms, the rivets have been the first to go.

8. The welded bottoms, being one piece, are absolutely tight.

9. The cost of scaffolding under the roof for the use of riveters is eliminated; with a welded roof, it is unnecessary to have any one underneath, which is a great advantage in hot weather.

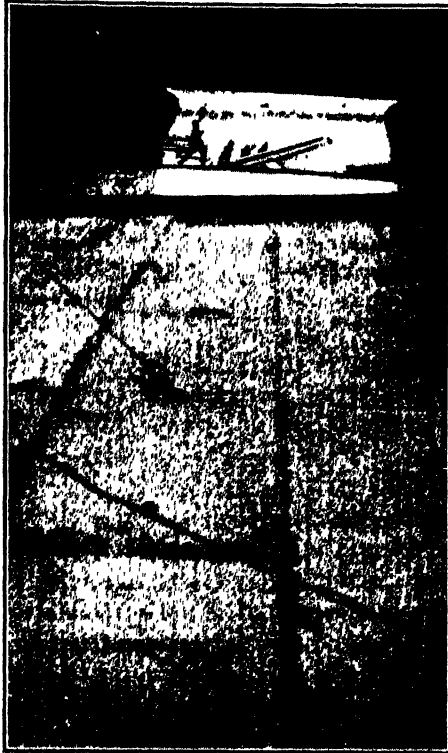


FIG. 12.—WELDED BOTTOM, SHOWING SMOOTH CONDITION OF PLATES AFTER WELDING.

#### FUTURE APPLICATIONS OF WELDING

Naturally, the next step to be taken in tank welding will be the welding of the shell. One can expect to hear any time of this being attempted. The greatest difficulty in the welding of a shell will be in the assembling and tacking. A shell with the vertical seams welded inside and out should certainly develop a greater strength than one of riveted construction.

Another use for electric welding in tank construction is in the replacement of worn-out bottoms. Heretofore, where the bottom has been

completely worn out, it has been necessary to build a concrete bottom or, if a steel bottom is desired, to tear down the tank, put in a new bottom and re-construct it. By the use of electric welding, the tank can be cleaned, a sheet cut out of the first ring, new plates dragged inside of the tank, set in place, and welded. The sketch plates can be welded on top of the bottom leg of the angle iron.

The writer wishes to acknowledge the assistance of V. T. Moon, chief engineer of the Marland Refining Co., from whom were obtained the data relative to the tests made on the welded roofs; also the assistance and coöperation of the engineers and executives of the Chicago Bridge and Iron Works and the Graver Corp'n. in the developing of methods for the assembling of roofs and bottoms.

## DISCUSSION

E. P. JESSOP, New York, N. Y.—The Navy Department has been prevailed upon to put into its specifications the authorization to weld tanks completely. The 150,000-bbl. tanks recently erected in Portsmouth, N. H., have electric-welded roofs and bottoms; they did not weld the circumference.

It must be remembered that welding today is not the unreliable thing it was a few years ago. When properly applied, the average welder, using proper equipment and method, will average 90 per cent. strength in a joint, as against about 72 per cent. for treble riveted, 64 per cent. for double riveted, and from 30 to 40 per cent. single riveted. The strength is controlled by the ductility much more than by the tensile strength. You can get tensile strength easily, but ductility is a measure of the ability of the equipment used and of the operator to handle the metal; in other words, it is a metallurgical condition. It is possible almost to destroy the material and still get almost full tensile strength on a test, but the metal is crystal hard and will stand no vibration or buckling and would be practically useless in the oil industry. With the short arc, as described by the author, you get a ductile metal and, at the same time, full strength. He used only a  $\frac{1}{8}$ -in. weld on his roof and yet had plenty of strength; no matter how much additional metal he would have added, he would have gotten little more strength because welding at the joint fuses the two pieces together and the greater part of the strength comes through this rather than through the amount of welding material added to the outside. The waste of welding wire is great because people believe that the more metal is put on a joint the stronger is the joint. If laid in with the proper method sufficient welding metal is about half the fillet on a double-welded joint. But even less than that may be used and still decrease the strength very slightly, as the two plates are fused together by the arc in addition to having the welded material there.

But the point is that if a welded joint is two-thirds stronger than a riveted joint, or one-third stronger, as the thickness of the metal in the tank is determined by the fact that the single-riveted joint is only 50 or 60 per cent. efficient, usually nearer 50 than 60, it is possible to save 25 per cent. of the material on an all-welded tank and get a stronger tank and one that is gas-tight. So that welding, in the oil industry, gives three things: lighter tanks, if you want them; gas-tight tanks, and tanks that require practically no upkeep. These three things make welding the natural method of assembling tanks that are assembled for permanence and not for just over night.

II. A. WHEELER, St. Louis, Mo.—How about the cost?

E. P. JESSOP.—The cost is very nearly the same as the riveted cost. At Portsmouth, I think the contract price was \$70,000; we estimated that between \$700 and \$1000 would have been saved if the entire tank had been welded. But original cost is a lot less important than it seems to be. A welded tank is a so much better tank that it will save you money in the long run; it is gas-tight.

II. A. WHEELER.—You do not rivet the vertical shapes?

E. P. JESSOP.—I would weld the whole thing, but I would not let an unskilled man do it. It is possible to get 100 per cent. strength in a welded joint, but the average joint will run probably between 85 and 90.

II. A. WHEELER.—How about burning the riveting steel?

E. P. JESSOP.—The equipment enters into that. Burned steel becomes evident at once to any engineer that is on the job. They burned some plates on the tanks in Portsmouth but the fact was so apparent that a novice could see it. Visual inspection will tell you that. People say it is not possible to test a welded joint; you can test it the same way as a riveted joint.

The reason I am so sure of what I say is that, in 1917, we did \$273,000 worth of welding on the German ships in the Port of New York and not one of those welds has gone bad. They are all electric-arc welded. But any company that is planning to do this work on a big scale should have in its employ some one who knows welding; you cannot do it carelessly.

II. A. WHEELER.—Is the welding metal a high-carbon steel?

E. P. JESSOP.—Its composition depends on the kind of work you are doing. The metal in this work would be a steel that would run strong in manganese so that, after going through the arc, it would still have sufficient manganese to give it the proper toughness. It is also high in carbon.





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# BIOGRAPHICAL NOTICES

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## Albert Reid Ledoux

IN THE Alumni catalogue of Amherst College and with the Class of 1848 is recorded the name of Louis Palemon Ledoux, who on graduating studied for the ministry at the Union Theological Seminary in New York and was ordained by the Presbyterian church. Louis Palemon Ledoux entered college from Louisiana and, as his name implies, was of French ancestry. His departure from the traditions of his forebears in registering in a Protestant college and later becoming a Presbyterian minister brought about some alienation from his family which, however, softened with the passage of years and disappeared between later generations. In time the Rev. Louis P. Ledoux was married to Kate C. Reid of New York City and was stationed for a year at Newport, Ky., where on Nov. 2, 1852, his oldest son, Albert Reid Ledoux, was born.

The next year the family moved to Monroe, Mich., where for two years the young clergyman was pastor of the Presbyterian church. A call to Richmond, Va., led them to live from 1855 to 1858 in the Virginia capital, but the father became afflicted with what was then regarded as a mysterious ailment, malaria, and to escape it migrated in 1858, when Albert was a little over five years old, to Cornwall-on-Hudson, and became pastor of the Presbyterian church in the lower village near the river. In 1861, he was honored with the degree of D.D. from the State University of Indiana. Some years later throat trouble compelled the Rev. Dr. Ledoux to give up preaching and led him to establish a school for boys, known as the Storm King School, above Cornwall, on the slopes of Storm King Mountain.

As a boy, Albert Ledoux roamed the woods of Storm King and became deeply attached to this wonderful hillside, commanding as it does an extended view of Newburgh Bay to the north and the remoter reaches of the Hudson. In his later years, he built his home on its slopes and continued to roam its woods for his recreation. In later years, also, the writer used to look each October for the fringed gentian which Doctor Ledoux gathered in some secret nook to wear in his lapel. In the Storm King school, Albert Ledoux and his brother Augustus Damon, seven years younger, were educated and then entered the School of Mines of Columbia College.

The older brother began his studies in 1870 and was thus a member of the class of '74, but at the end of three years he resolved to go abroad for study, and matriculated in 1873 at the University of Berlin, where he pursued courses in chemistry, mineralogy, and physics. While in

Berlin, he was a roommate and chum of Elihu Root, a brilliant young student of physics from Amherst College, who, after taking his Ph.D. with high honor under the famous Helmholtz, became professor of physics in his alma mater and an exceptionally inspiring teacher of the few young men, among them the writer, who came under him during the brief four years of his professorial life. After two years in Berlin, Albert Ledoux migrated to Göttingen, which was the university where most of



ALBERT REID LEDOUX.

the American students in Germany in the middle decades of the last century made their doctorates. Completing his in 1876, Doctor Ledoux, as he was ever afterwards known, returned to his home and found a place in the laboratory of William M. Habirshaw, a practicing chemist and assayer in New York.

The following year the State of North Carolina established an agricultural station of which Doctor Ledoux was appointed director and was made at the same time State Chemist. His headquarters were at Chapel

Hill, in connection with the State University. For four years he served the State and on his resigning and coming north again in 1880, the State University gave him the honorary degree of M.S. During these years Doctor Ledoux had not remained entirely absent from Cornwall, but had been married to Annie Van Vorst Powers, the daughter of one of his old neighbors. Cornwall was indeed at this time a little community, but contained some families distinguished in the literary life of the country. It was the home of Nathaniel P. Willis and of the Rev. Lyman Abbott, already a leader in the liberal religious thought of the day. Amelia Barr resided there, as did E. P. Roe, the author of several widely read novels, quite distinctly characteristic of that period in our literary history. The construction of the Ontario & Western R. R. and of the West Shore, on the former's right of way to this point, soon after brought the village in direct railway communication with New York, or at least with the Jersey shore across the river.

In April, 1880, Doctor Ledoux opened an office and laboratory for the general practice of analytical chemistry and assaying, in association with the late Pierre de Peyster Ricketts, then instructor in assaying in the School of Mines. The firm name was at first A. R. Ledoux & Co., but soon after became Ledoux & Ricketts. After five years it was dissolved and Doctor Ledoux established Ledoux & Co. with his younger brother Augustus forming the "Co." Later, the firm was incorporated under the same name and the shares of the corporation were distributed among the members of the technical staff.

The firm of Ledoux & Co. in a very short time acquired a reputation for reliability and straightforward dealing which commanded confidence in the highest degree. Every question or criticism raised by a client was met at once with the fullest and frankest treatment and no effort was spared to fulfill obligations in such a manner that reasonable people would be more than content. Gradually the sampling and assay of high-grade copper ores, passing through New York for export, of matte and crude metal on the same journey, came to pass very largely through the firm's laboratory. A sampler of their own was required for this purpose and of its establishment alongside the Erie R. R. tracks just west of Bergen Ridge, Doctor Ledoux has written a very interesting account in the second of his three "Technical Reminiscences" in the *Mining and Scientific Press*, for May 29, 1915. The United States was exporting in that decade a very large and growing amount of the red metal. The reminiscence account given by Doctor Ledoux, in the reference cited, of the way foreign buyers were induced to accept the American assays of his firm and to do away with the tedious and antiquated methods of Swansea, constitutes a chapter of no small importance in American metallurgy.

The firm also did examination work on mining properties and Doctor Ledoux was often in the West, in Mexico, and in Canada on these errands.

Perhaps in no other profession does an engineer have so many interesting experiences as in mining. He comes in contact with all sorts and conditions of men, and in relations which bring out all the good and all the bad sides of character. There are inevitably so many chances involved in mining, that sound judgment, keen understanding of human nature, geological good sense, and familiarity with business and labor conditions are all involved. Poise and the judicial way of looking at things are especially requisite: sometimes also personal courage and quick decision. In the mines and the remote camps the engineer must meet the miners on the broad, human foundation of good fellowship; and in the office or home of the capitalist he must be the well-bred man of the world. Rarely is so happy a combination of these qualities met as in Albert R. Ledoux. In the other two of the three contributions, "Technical Reminiscences" of which one was cited above,<sup>1</sup> we go with him from the library of Baron Alfred de Rothschild in London to a buggy ride across the plains of northern Montana into the Sweet Grass Hills with James J. Hill of the Great Northern; and thence to watching the peons panning out stray amalgam in the creek sands of Pachuca. These reminiscences are themselves the written-out form of an after-dinner address to students of geology made at the writer's request in May, 1913, on which occasion Doctor Ledoux found himself face to face with a menu card in the Chinook jargon, and headed "Tahtlelum Hy-iu Muckamuck pee Wau-wau." We furnished the Hy-iu Muckamuck,<sup>2</sup> and he came back with Hy-iu Wau-wau.<sup>3</sup>

On the trip, moreover, into the Sweet Grass Hills, Doctor Ledoux did not fail to bring back geological observations of interest and value, which were duly recorded in the *Transactions* of the New York Academy of Sciences.<sup>4</sup> Indeed, not infrequently in conversations with the writer, some observation by Doctor Ledoux would come up, which was of significance and suggestiveness.

In matters closely akin to metallurgy Doctor Ledoux was often called on for expert advice. Thus for the first projected placing of all the telegraph and telephone wires in a subway in New York City, when insulation was far less developed than now, he was retained as consulting engineer. On the stand, in disputes before the courts involving technical questions, he often served as expert witness and always with clear and intelligible testimony which carried weight for its sound information and good sense.

In many relations in life, he was chosen as arbiter or referee for the settlement of disputes or the straightening out of difficult situations. They were always met with great evenness of disposition and with an

<sup>1</sup> *Min. & Sci. Pr.* (1915) 761-763, 903-907.

<sup>2</sup> Plenty to eat.

<sup>3</sup> Plenty of talk.

<sup>4</sup> Vol. 10 (1891) 59, and freely quoted by the writer in *Bulletin of the Geol. Soc. of America* (1921) 32, 443.

intuitive sense of justice. Over and over, his decisions were taken as the final word. One of his most important professional engagements was the receivership of the Harney Peak Tin Mining and Milling Co. of the Black Hills, an ill-advised and disastrous venture, which presented a difficult tangle to unravel. An account of the case was written by him for the *Engineering and Mining Journal* of July 7, 1894.

Doctor Ledoux became a member of the American Institute of Mining Engineers in 1889, and entered vigorously into its work. He served as manager, 1895-97, by which title the members of the council were called under the constitution of the time; as vice-president 1898-99 and 1919-25, having at the time of his decease still two years of unexpired term. He was president in 1903. He was one of the nine incorporators, in 1904, and became thereby a director of the corporation when the certificate was issued Dec. 30, 1904. During the last 25 years he has been a member of almost all the important committees, and was so manifestly the man for the place that his selection went almost as a matter of course. At the monthly dinner and meeting of the Directors he was one of the most faithful in attendance and in the discharge of his duties. In the year 1923 he was chairman of the committee to coöperate with the Canadian Mining Institute; member of the Advisory Committee on MINING AND METALLURGY, and most important of all, chairman of the Executive Committee. In this connection we may recall that he was also a member of the Executive Committee of five, which served without change in personnel through three administrations in the trying and critical years 1912, 1913 and 1914. Of his invaluable services at this time in keeping the great organization intact, too high and too emphatic praise could not be put into words. One of his last and most graceful services was rendered as Chairman of the James Douglas Medal Committee, whose first award was made at the last Annual Meeting (1923).

Doctor Ledoux was a member of many other technical societies, of which the Mining and Metallurgical Society, and the Canadian Institute of Mining and Metallurgy may be specially mentioned. At the meetings of the Canadian Institute, he was for years a familiar and welcome figure. He entered alike into the serious exercises and into the merry-making. My mind goes back as I write to the session in Quebec, in March, 1911, when he served as trial attorney for the accused, in a famous mock breach-of-promise suit. The whole frolic was so absurd and so wittily conducted that no participant or on-looker can recall it even to this day without smiling and smiling to himself. One other incident of the meeting may be recorded. Doctor James Douglas was in attendance. Quebec was the home of his boyhood. Of the old city, as everyone knows, we have a delightful volume written by him *con amore*. The Monseigneur in charge of the Laval University was his boyhood playmate and friend. Doctor Douglas invited Doctor Ledoux, W. R. Ingalls, and the writer to



spend the afternoon visiting this ancient seat of learning, established in the new world by France in its colonial days. With the gentle and lovable Monseigneur we were all four transported back through the centuries as we walked its corridors and viewed its treasures of portraits and mementoes of by-gone days.

Doctor Ledoux was a man of deep and thoroughly natural religious life. His religion was the unforced expression of the beliefs and the faith which were fundamental in his nature. Reared in his youth in this atmosphere, he created it about him as he left his parental home for his own career in the world. On settling in New York he became connected with the Brick Church of the Presbyterian communion, at Fifth Avenue and 37th Street. He entered actively into its work and at his decease was its senior Elder in term of service and could count more than 40 years in its membership. The Brick Church is one of the famous old religious foundations of the city and has been for over a century one of its strongest bodies. For many years the Rev. Henry Van Dyke was its pastor and during those years a strong friendship sprang up between him and Doctor Ledoux.

Doctor Ledoux was also a man of not a few other strong and devoted friendships. Genuine, frank and open himself, he attracted to himself others whose make-up craved these qualities in their friends. He did many unobtrusive and generous acts to members of the vicissitudinous profession of mining engineering, with its many ups and downs of fortune and its over-severe demands upon those who pass three score years and ten. At Cornwall-on-Hudson, where he always felt and said he had his real home, he was known as one of the most public-spirited and generous citizens of the community.

Doctor Ledoux's final passing on Oct. 25, 1923, was unexpected by those nearest him. He had been on a trip for recreation to the woods of Canada, but on his return developed some obscure and not fully understood ailment from which after returning to Cornwall, he peacefully and quietly sank into the final sleep.

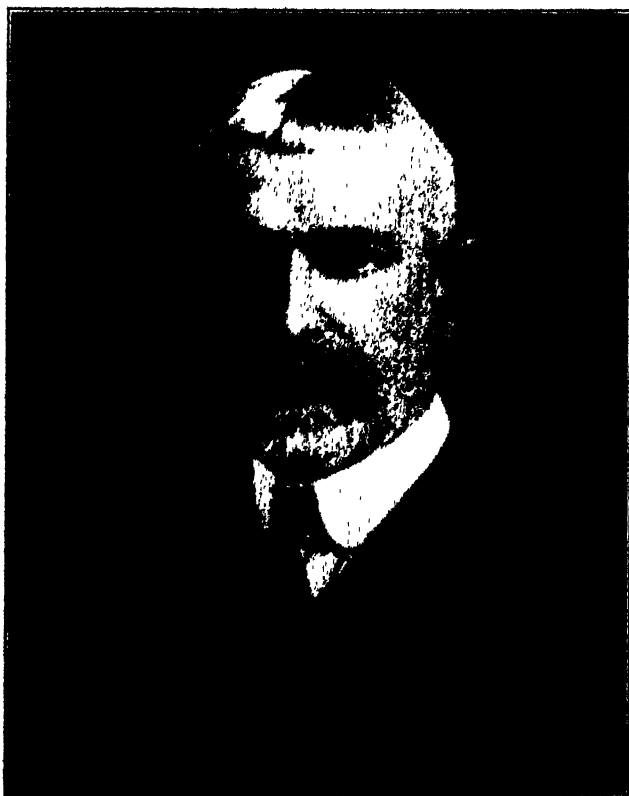
Doctor Ledoux leaves one son, Louis Vernon, who was born in New York soon after his father moved to the city from North Carolina. After pursuing in college and professional school the studies qualified to prepare him for entrance into Ledoux & Co., Louis Ledoux became active in its work.

Doctor Ledoux was twice married. In 1918 the companionship of many years was broken. Recently the loneliness of his life and home was dispelled by his marriage in London to Mrs. Alice Benet Baird, who survives him. Doctor Ledoux also leaves two grandchildren, Renée and Louis Pierre, 15 and 11 years of age. The profound sympathy of the Institute goes out to his family.

JAMES FURMAN KEMP.

## Edwin Ludlow

EDWIN LUDLOW, the forty-first President of the A. I. M. E., died in Muskogee, Okla., on Feb. 10, 1924, after a brief illness of influenza followed by pneumonia. He was born in Oakdale, N. Y. (on Long Island), March 12, 1858, a son of William Handy and Louise (Nicoll)



EDWIN LUDLOW.

Ludlow. He attended Flushing (L. I.) Institute 1868-75, and Columbia School of Mines (N. Y.) where he was graduated with the degree of Engineer of Mines with the Class of 1879.

After graduation, his first employment was as assistant engineer in river and harbor work on the Delaware River near Philadelphia. In

1881, he went to Mexico as one of the engineers on the Mexican Central Railroad, then building from Laredo, Texas, to Mexico City. The road being in financial difficulties, he returned to the United States, and shortly thereafter was made superintendent of the Union Coal Company's collieries in the western middle anthracite field, between Shamokin and Mt. Carmel.

Edwin Ludlow and Arthur H. Storrs, then superintendent of the Neilson Shaft Colliery, in Shamokin, were known throughout that section as the baby superintendents, both under 25 years of age. The appointments of such young men were at that time unique and set a record for youthful assumption of responsibility in the region. One of Ludlow's exploits, which his old associates loved to tell, was the rescue of a team of mules caught by a sudden inflow of water; while the old bosses were bemoaning the loss of the mules, the young superintendent stripped and swam through the flooded gangway and brought them out. In 1885, when Irving A. Stearns was made manager of the anthracite properties controlled by the Pennsylvania Railroad Co., he made Ludlow superintendent of the Mineral Railroad & Mining Company's properties, the Camoron and Luke Fidler collieries at Shamokin.

In 1889 Edwin Ludlow was offered charge of the properties of the Choctaw, Oklahoma and Gulf R. R. Co., virgin coal lands at Hartshorne, Okla. The opportunity to open and develop this great property, a field 80 miles long, appealed to the brilliant young engineer, and he left the East to make his home and fame in 22 years of arduous and successful work in the Southwest. Leaving Oklahoma in 1899, he became general manager of the Mexican Coal & Coke Co., Las Esperanzas, Mexico, which he operated with notable success until he left the country in 1911.

In Oklahoma, Mr. Ludlow met his wife, Miss Anna Wright, whom he married on Nov. 22, 1893. Her delightful personality and open-handed hospitality, which, through the years, has added so much to its affairs, was first experienced by the Institute when the entire party was entertained at Las Esperanzas during the Mexican meeting of 1901. At that meeting Mr. Ludlow presented an able paper on the coal fields of Las Esperanzas, Coahuila, Mexico, describing in detail the geology of the field and the mining methods and plant of the company.

The opportunity to return to the East as vice-president and general manager of the New River Collieries Co., at Eccles, West Va., tempted him in 1911 to leave Mexico. A year later, W. A. Lathrop, then president of the Lehigh Coal & Navigation Co., induced Mr. Ludlow to return to his first mining work in the anthracite region, as vice-president and general manager of that company, unquestionably the oldest incorporated coal company in the United States. From 1912 to 1919, he brought his great abilities and ripe experience to the upbuilding of this old company. Its tonnage increased from 3,674,000 in 1912 to 4,763,000 in 1919; but that

this increase was not at the expense of careful work is shown by the reduction in the fatal accidents' rate from one to each 160,000 tons produced in 1912 to one to 235,000 tons in 1918.

Although wishing to retire from the burden of great operations, Mr. Ludlow patriotically subordinated his wishes to the national need and remained in charge until after the War. Then he entered consulting practice in New York, and up to the time of his death continued in that practice and in looking after mining interests in Oklahoma, where he was heavily interested.

Mr. Ludlow became a member of the Institute in 1893; served as Director 1916-19, Vice-president 1919 and 1920, First Vice-president 1920, and succeeded Mr. Hoover as President in 1921. That year he largely devoted to the service of the Institute. He was vice-chairman of the Anthracite Section from its inception until he left the region. Besides his Institute honors, he was an honorary member of the Institution of Mining and Metallurgy of Great Britain, and a member of many American technical societies. As a Columbia graduate he was honored as Director and, in 1919 and 1920, President of the Alumni Association of the Schools of Mines, Engineering and Chemistry, and served for years on the board of the Columbia Alumni Federation.

An engineer of high attainments, he was also an executive of the front rank, notable for both his organizing and his operating ability. A great believer in young men, he encouraged his subordinates to record their work, and to his suggestion and assistance are due the valuable papers presented to the Institute during recent years from the district dominated by his company.

Always fond of his fellow-man, Mr. Ludlow belonged to many social organizations, the University, Century, Columbia University and Downtown Clubs in New York, the Engineers' Country Club on Long Island, the Muskogee Oklahoma Country Club and the United States Seniors Golf Association.

Edwin Ludlow came from an old New York family; only very recently they sold their Long Island homestead, the only prior conveyance of which was from the Indians to a direct Ludlow ancestor. Mr. Ludlow was the last of his name, his two older brothers, Admiral Ludlow, and General Ludlow, formerly Governor of Cuba and of the Philippines, are without male descendants. Surviving him are his widow; one sister, Mrs. Robert Bond of Fort Smith, Ark.; and a host of friends from the Atlantic to the Pacific and from Mexico to Canada who will sorely miss him.

In the minute recording his death the Board of Directors of the Institute said:

In his death the profession loses a courageous leader, strong in his convictions, honorable in his dealings, competent and trustworthy in his work, loyal in his friendships and eloquent in upholding its best traditions.

R. V. NORRIS.

## Christopher Robert Corning

CHRISTOPHER R. CORNING was one of the ablest mining engineers and geologists in America and one whose name was well known also in Mexico, Cuba, South America and many European countries. He was educated at Zurich, Switzerland, and at the Bergakademie, Freiberg, where he was graduated in 1883 with the degrees of Markscheider and Bergingenieur. He continued his studies at Heidelberg until 1886, chiefly in chemistry, under Bunsen, and mineralogy and petrography under Rosenbusch. Although he received a Ph.D. in chemistry, he never used the title. During holidays of 1883-86, he traveled, seeing mines and studying geology in Spain, France, England, Italy, Germany, and Austria.

In 1886, he returned to America and in 1887 he was in the Lake Superior iron ore country on the staff of John F. Stevens, then building the Duluth South Shore and Atlantic Railway. In 1889, Mr. Corning was at the Bunker Hill & Sullivan mines at Wardner, Idaho, with John Hays Hammond, and there met E. E. Olcott. Although Mr. Corning was not long connected with the Bunker Hill & Sullivan mines, he left the imprint of his ability and splendid personality upon the men and the property. That his friendship was cherished was manifested by the cordiality, hospitality and frequency of letters of good counsel and cheer.

In 1897, Mr. Corning, with E. E. Olcott and Prof. Robert Peele of Columbia University, formed the firm of Olcott, Corning & Peele, consulting mining engineers. Pressure of university duties compelled Professor Peele to withdraw in 1904, and later Mr. Olcott was forced to retire by reason of other important business interests, but the friendship and high mutual regard of the three men continued undiminished. About 1902, Mr. Corning and Professor Peele translated into English Riemer's book on "Shaft Sinking under Difficult Conditions."

Mr. Corning's knowledge of structural geology, mineralogy and ore deposits was extensive and accurate. He was a close and intelligent observer. When he became interested in a problem, no amount of trouble was too great in endeavoring to reach a satisfactory solution. He had professional experience in the West, notably in the Coeur d'Alenes, Mexico and South America, and several times was called on to attempt to straighten up mismanaged properties.

In 1912, at the request of a large number of members, Mr. Corning headed the "Committee of Five" that investigated the affairs of the American Institute of Mining Engineers and brought about beneficial changes in the organization and its policies. He was one of the organizers

of the Mining and Metallurgical Society of America and gave much thought to its affairs. He served eight years as a member of the John Fritz Medal Board of Award.

During the last ten years Mr. Corning maintained his office in New York as a consulting engineer.

Mr. Corning traveled extensively throughout the United States, Europe, Mexico, South America, and Cuba. He knew Europe thor-



CHRISTOPHER ROBERT CORNING.

oughly, was a master of many languages and had a knowledge of the literature thereof. He was a man of broad view and very far seeing. He had a mental poise and soundness of judgment that gave his opinion unusual value, often foreseeing with great accuracy the development of political and economic events. He had a penetrating, judicial mind. He despised vague opinions and rejected generalizations when it was at all possible to be definite and precise.

Mr. Corning was utterly truthful, straightforward and upright in character. He had high ideals and was impatient of looseness of statement and of humbug in all its forms. Sometimes he was so positive in expressing his opinion that he aroused antagonism among those who did not know him intimately enough to appreciate his sterling mental and moral qualities; a man of fine dignity with a splendid but practical conception of what is broadly referred to as professional ethics; intolerant of the shoddy incompetent characters that by chance might cross his path.

He was noted for loyalty and faithfulness to his friends. There was no sacrifice too great for him to make for one for whom he had a feeling of real friendship. One never seemed to get very close to him, however, even if one was much with him. He was ever the kind and courtly gentleman of the opposition. His peculiarity of strongly held opinions with a somewhat quick temper occasionally repelled men before they had an opportunity to understand him. He was always ready to give up his strong prejudices if they could be shown to be unfounded. He was most anxious to get at the truth. He tried to be fair. It took strong reasons to make him change his opinions, but he was willing to change. In reality, innate courtesy coupled with an earnest desire to do the right thing were so dominant as to be his controlling motives. With a kindly and affectionate nature, he responded to friendship in an almost boyish way.

Mr. Corning took a considerable interest in economic and political questions, which became greater as time went on. His tendency was toward pessimism; this seemed accentuated toward the close of his life and was often expressed by a directness of speech which amazed the hearer. After his stroke in 1922, a great change came over him, which surprised his friends. He became much milder both in his opinions and in his manner of expressing them. The patience with which he bore his long illness and the restrictions entailed thereby was wonderful.

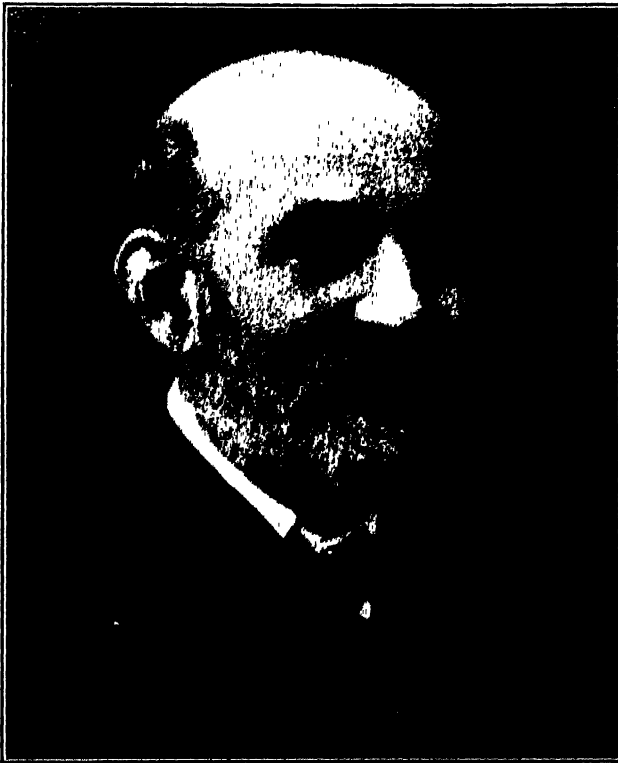
Mr. Corning was born in New York, May 12, 1859. He died at Châtel-Guyon, France, July 2, 1924. He is buried at Petit Saconnex, Geneva, Switzerland, near the residence of his sister, Mrs. Sarah C. Galopin. She and Prof. H. K. Corning, his brother, of Basle, Switzerland, survive. His father, Ephraim L. Corning, died at Litchfield, Conn., only one week before him. His mother died thirty years ago.

It may be truly said of Mr. Corning that he was a man it was a privilege to know. He was exceptional in his breadth of reading and though his favorite subjects were scientific he was acquainted with and appreciated a great range of English, French and German literature. He was essentially an aristocrat in a social and professional way. This characteristic combined with his others inspired a high professional ideal and an attitude that sometimes made him "difficult" with Americans; nevertheless, he was loyal, warmhearted and, with all his worldly experience, "true blue."

CHARLES F. RAND,

## John Edward Stead

JOHN EDWARD STEAD, a past-president of the British Iron and Steel Institute, and an Honorary Member of this Institute since 1906, died at his home at Redcar, Yorkshire, on Oct. 31, 1923, after a long illness. For many years, Mr. Stead had been recognized as a leading authority



JOHN EDWARD STEAD.

in chemical and metallurgical matters, particularly those relating to iron; he gave freely of his experience by the contribution of papers to the twenty-eight technical societies in which he retained his membership as recently as 1920. He had been honored with the Doctor's degree by three English universities, and was elected a Fellow of the Royal Society



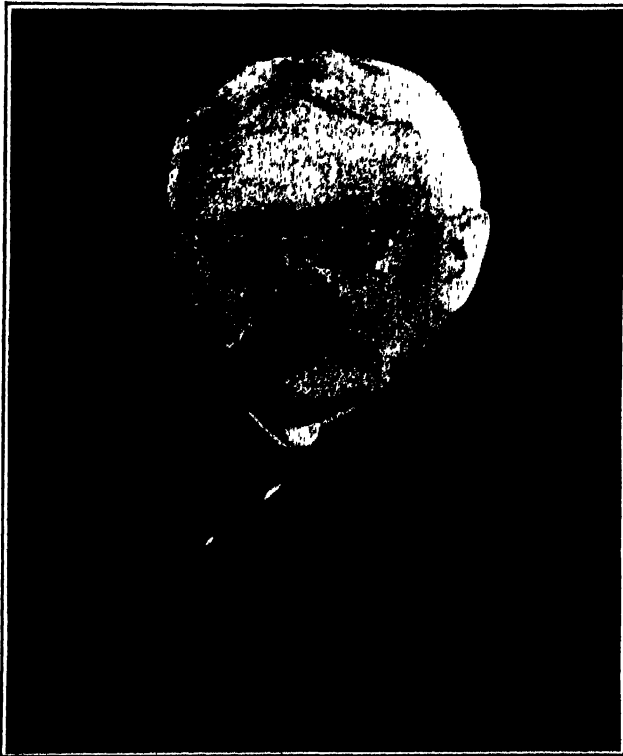
in 1903. The Bessemer Medal was awarded to him in 1901, by the Iron and Steel Institute.

Doctor Stead was born Oct. 17, 1851, at Howden-on-Tyne, and owing to his delicate health received his early education from his father. When sixteen years old he was apprenticed to John Pattinson, analytical chemist at Newcastle, with whom he entered into partnership in 1876, having meanwhile gained further practical experience as chemist for the Tharsis Sulphur and Copper Co., and for Bolokow, Vaughan & Co. In 1906, Mr. Pattinson retired, but Doctor Stead continued the practice under the same name, Pattinson & Stead, in partnership with H. Frankland.

In addition to his technical pursuits, Doctor Stead took active part in the civic, educational and philanthropic affairs of Middlesbrough and other districts of north Yorkshire.

## Heinrich Oscar Hofman

IN THE death of Professor Hofman, the world has lost a great metallurgist and a great author of metallurgical literature. Measured in time, his life was not quite seventy-two years, but measured in work accomplished it was much longer than this. He was born Aug. 13, 1852 and died Apr. 28, 1924.



HEINRICH OSCAR HOFMAN.

It is not surprising that Doctor Hofman became a great scholar, for his father, Karl Hofman, was on the faculty of Heidelberg University, and his early days were spent in those surroundings. He studied in the university under such men as Kirchhoff and Bunsen and often spoke of his

intimate relations with them. Following his course at Heidelberg, he studied at the Clausthal Mining Academy, where he was graduated with honors, receiving the degrees of Mining Engineer and Metallurgical Engineer in 1877.

After four years of practical work in Germany, Professor Hofman came to the United States and during the next four years was employed for brief periods successively by the Mine La Motte Co.; the Argentine Lead Works, Kansas; the Delaware Lead Works, Philadelphia; the Grand View Mining and Smelting Co., Rico, Colo.; and the Carmen Mining Co., Mexico.

In 1885, Professor Hofman was invited by Prof. R. H. Richards, head of the Department of Mining Engineering at the Massachusetts Institute of Technology, to give a course of lectures on lead smelting, and later during a brief period he substituted in teaching both mining and metallurgy. He remained at the Institute for two years as private assistant to Professor Richards, leaving in 1887 to become Professor of Metallurgy and Assaying at the South Dakota School of Mines. In 1889, he returned to the Massachusetts Institute of Technology as Assistant Professor of Mining Engineering and Metallurgy, and served successively as Associate Professor and Professor of Metallurgy. On the retirement of Professor Richards in 1915, he became head of the Department of Mining and Metallurgy. In 1922, having reached the age of 70, he was automatically retired with the title Professor Emeritus.

A year before he retired he suffered a slight paralytic stroke and by almost imperceptible degrees it became more difficult for him to get about. For several months before his death he was confined to his house.

In 1889, Professor Hofman received the degree Ph.D. from Ohio University and, in 1921, the American Institute of Mining and Metallurgical Engineers made him an Honorary Member.

Throughout the United States and other countries, Hofman's treatises on metallurgy will be found on the shelves of technical libraries, both public and private, and the *TRANSACTIONS* contain numerous papers by him. His first book, "Metallurgy of Lead," published in 1892, at once became a standard work. It ran through several editions and was completely rewritten in 1918. This book, together with various papers on the subject and annual reviews in the *Mineral Industry*, established him as one of the foremost authorities on lead in the country. As chairman of the Lead Committee of the Institute, he was in continual touch with the progressive men in the industry and urged them to publish the results of their experience and research. In this way he made an indirect though important contribution to the literature of the subject. His "General Metallurgy," published in 1913, has been translated into several languages. "The Metallurgy of Copper" followed in 1914, and "The Metallurgy of Zinc and Cadmium" in 1921. It had been his ambition to

complete the series by a volume on "Minor Metals," another on "Gold and Silver," and possibly a volume on "Iron and Steel."

A reader of the Hofman books is at once struck by the profuse bibliography. Authorities are given for every statement and each subject is viewed from all angles. For many years, his desk was in the departmental library and he was familiar with every book on its shelves. All the world's leading publications on mining and metallurgy passed through his hands and important articles were noted and catalogued. He had a remarkable memory for published facts, and times without number the inquiring student was given a reference where he could find an answer to some question.

It was Professor Hofman's custom to take about a month in the summer for vacation. During the remainder of the year, except when engaged in classes or routine school work, he was poring over his manuscripts in various stages of preparation. His power of concentration was a marvel to his associates. He would work in the library for hours amid a pile of reference books and bound periodicals, apparently oblivious to students coming and going around him. After putting the manuscript of a book in the form of a rough draft, it was his custom to visit most of the leading smelting plants and then with fresh information in hand put it into final form. He also carried on an extensive correspondence with friends in the industry who kept him informed on recent progress. The results of these painstaking efforts to secure accuracy and to completely cover the field are fully evident in his books. Few men have the qualifications necessary to produce such treatises.

Although Professor Hofman had a host of friends and acquaintances and was known by reputation to a still larger group, it is doubtful if a large number knew him as a man apart from the metallurgist. This was true even with most of the students in his classes; all of them respected him, but only a small number sought his friendship. To this inner circle there was revealed a kindly nature and a sympathetic spirit. Here was a man who had at instant command a wonderful store of knowledge yet a remarkable simplicity of manner which removed all embarrassment and allowed free interchange of ideas on a plane of equality and comradeship.

Professor Hofman was well informed on public affairs and kept familiar with the best literature. He was passionately fond of music and for years was a regular attendant at the concerts of the Boston Symphony Orchestra. These tastes were shared by his wife and served to produce a pleasant home atmosphere and a restful change from the arduous technical duties of the day's work.

At the outbreak of the World War, Professor Hofman clearly discerned its causes and his sympathies were entirely with the Allies from the start. It was a trying period for him, with nephews serving on both

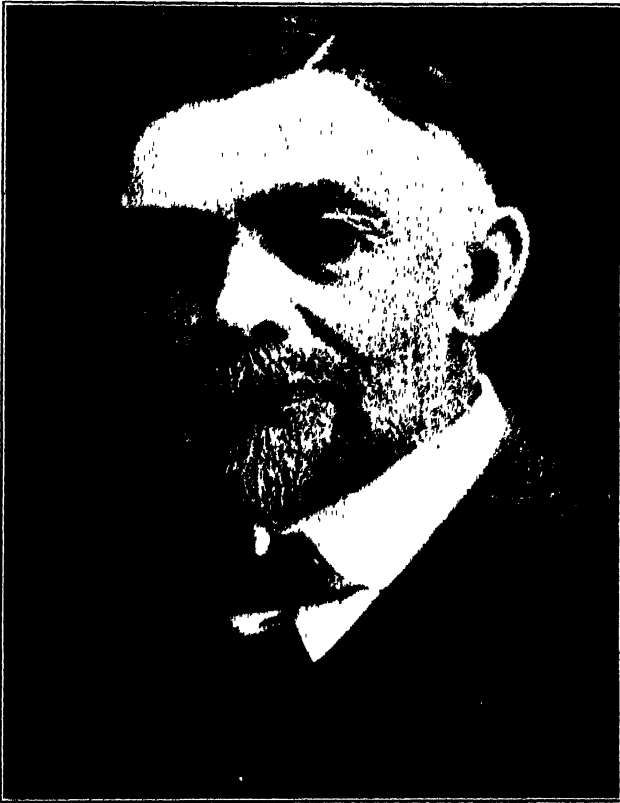
sides, but there was never a doubt regarding his attitude toward Prussian militarism.

Professor Hofman was married, in 1883, to Josephine Loughhead of Philadelphia, who died after a few years; and, in 1902, to Fannie E. Howell, of Boston, who survives him, as do also a son and a daughter. The son is now a student at the Massachusetts Institute of Technology. As the technical world loses a commanding figure, they mourn one who was in every sense a loving husband and father.

CARLE R. HAYWARD.

## Fred Walter McNair

THERE is mitigation for the sorrow of friends and the tragedy of sudden death when that death comes at the height of a successful career. It is not everyone's privilege to die, as has been the wish of many, in the harness—toiling, accomplishing, still necessary to the scheme of things. Nor is it everyone's privilege to leave a monument to his work.



FRED WALTER MCNAIR.

Dr. Fred Walter McNair died thus—in the midst of his work of educating, leaving along the path down the quarter century of his presidency of the Michigan College of Mines hundreds of men who, having come under his influence, have been successful in life.

After graduating from the University of Wisconsin and studying at the University of Chicago, Doctor McNair went first to the faculty of the Michigan Agricultural College. In 1893, as a young man only two years out of college he was sent to the Michigan College of Mines as head of the Department of Mathematics and Physics. Six years later he was made president, when the institution consisted of but two buildings and the idea of mining engineering colleges was still new. Today, after twenty-five years of his unflagging, loyal effort, ten buildings house the College of Mines, which has a world-wide reputation.

In his father before him were the roots of his great ability as an educator and his deep devotion to education, for it was H. A. W. McNair who, as chairman of the Legislative Finance Committee, brought about co-education at the University of Wisconsin, an idea which did not find ready approval at the hands of the slow-thinking pioneers of the early days.

Doctor McNair's ability as a physicist was widely known but his hope that he might some day spend all his time in physical research was never consummated; his executive duties were too pressing. His hobby was Nature. In his early days it was the minerals of northern Michigan in which he was interested. He found Powellite for the third time in the world and in an entirely new crystal formation. In later years it was myxomycetes and he contributed to the authority, MacBrides' book on the subject.

Upon the entry of the United States into the War, Doctor McNair made the college campus an army post, and it was there that the engineer battalion of the 32nd Division was recruited and trained. From his own duties in Washington he frequently went back to see the little army which he loved to think of as his own. His war activities, however, were among the colleges as well, for in 1917, acting on a suggestion of the War Department, he organized a committee which united forty-one leading engineering colleges of the country in a publicity campaign—the first instance of such college coöperation.

The greater part of his time during the War and the year following was spent in Washington and with the Pacific Fleet. Two of his life-long friends collaborated with him in developing for the United States Navy a revolutionary instrument for the big guns in the next war. That the finer, more technical, more important engines of war must be kept secret lest an enemy profit, is the reason why the world has not known of this contribution to naval gunnery.

Doctor McNair was a member of the Joint Conference Committee established by the National Industrial Conference Board for the study of engineering education as related to industries. He engaged in various expert investigations for private interests, and was a contributor on physical, engineering, and educational subjects to technical and scientific

periodicals. He was a member of the American Physical Society; Fellow of the American Association for the Advancement of Science, vice-president, Section D, 1904-05, secretary of council, 1905-06, general secretary, 1906-07; member Society for Promotion of Engineering Education, member of council, 1900-02, vice-president, 1902-03, president, 1904-05; member, American Institute of Mining and Metallurgical Engineers, Mining and Metallurgical Society of America, Lake Superior Mining Institute, Phi Beta Kappa, Tau Beta Pi, Rotary, and various other clubs.

Fred Walter McNair was born at Fennimore, Wis., on Dec. 3, 1862. He was killed in a railroad accident at Buda, Ill., while returning from the annual meeting of the Society for the Promotion of Engineering Education.

HUGH MCNAIR.



## Raphael Pumpelly

RAPHAEL PUMPELLY, who became a member of the Institute in 1871, the year of its organization, and retained his membership for a long period, died at his home in Newport, R. I., Aug. 10, 1923. He is survived by a son, Raphael, Jr., and by two daughters, one of whom is the wife of Prof. Henry L. Smyth, of Harvard.

Doctor Pumpelly was born in Oswego, N. Y., in 1835. He studied sciences and mining engineering in Paris and at Freiberg, later taking his Doctor's degree at Princeton. He was Professor of Mining at Harvard from 1866 to 1873.

Doctor Pumpelly made geological explorations in many lands. In 1861-63, he conducted a scientific exploration for the Japanese government, and for two years thereafter carried on researches in central, western, and northern China and Mongolia. In 1864-65, he undertook a voyage of exploration across the Gobi desert, returning to Europe through Siberia.

He was State Geologist of Michigan from 1869 to 1871; Director of the Missouri Geological Survey from 1871 to 1873; and Chief of Division, U. S. Geological Survey, directing the mineral industries division of the tenth census. He organized and directed the Northern Transcontinental Survey, 1881-84; directed the explorations inaugurating the iron ore industry of most of the ranges of Michigan and Western Ontario, 1897-1901; initiated and directed a physical-geographical and archeological exploration of Central Asia under the auspices of the Carnegie Institution of Washington, 1903-04.

## Oscar Rohn

OSCAR ROHN was born in Jackson, Wis., June 27, 1870. He attended the University of Wisconsin and there gained from Professor Van Hise his inspiration for scientific effort and useful attainment. While a student



OSCAR ROHN.

at Wisconsin he was interested in athletics and was a member of the first eight-oared crew that Wisconsin sent to compete with Eastern crews at Poughkeepsie. He was an instructor in the gymnasium for several years. He received his B. S. in 1895 at Wisconsin, specializing in engineering and geology.

In 1898, he was a member of a reconnaissance party in southwestern Alaska, under Mr. Spurr.<sup>1</sup> In 1899, he was in charge of a detachment of the Copper River Military Exploring Expedition sent out by the U. S. War Department. Mr. Rohn's report on the geology of the Chitina River and Skolai Mountains, Alaska, explored during this season,<sup>2</sup> was a reconnaissance report, but its accuracy was testified to many years later by Moffit and Capps in a more detailed report for the U. S. Geological Survey on this same region.

From 1901 to 1903, he was active in mine management and in exploration for iron ore in the Lake Superior region. During 1902 and 1903, he was manager of the Donora Mining Co. At about this period, he made a geologic study of the Baraboo iron range, acquired a large acreage of iron lands and developed an iron property that became one of the producers of that district. From 1903 to 1906, he carried on work as a consulting engineer. In 1903, he made an extended examination of properties in Cerro de Pasco, Peru. From 1904 to 1906, he was engaged in examining mining properties in Tonopah and Goldfield and other mining districts of Nevada. He organized and operated an automobile stage line in this territory, which served as a connecting line between various railroad points and isolated mining camps.

In 1906, he went to Butte, Mont., as manager of the Pittsburgh and Montana Copper Co., which had a large acreage east of the principal mines of the Butte Hill. Its property, known as the Pittsmont mine, had two shafts sunk to the 1200-ft. level and a considerable amount of development work done at this level. It also had a smelting plant. As to ores in sight, however, the property was sadly deficient. Indebtedness in bonds and notes amounted to nearly three million dollars. Mr. Rohn recognized the importance of the secondarily enriched ores of the higher levels in the Butte camp. He had also been told by Malcolm MacDonald that the Silver Bow mine of the Anaconda company, where it reached the west boundary of the Pittsburgh and Montana ground, had left standing at the boundary line a fine shoot of ore on the 800-ft. level. In the early development of the Pittsmont, drifts had been run a long distance to the west on the 1200-ft. level of this property. Mr. Rohn carried these workings to a point near the west boundary, raised and equipped for hoisting a three-compartment vertical shaft to the 800-ft. level, and there found a shoot of ore that put the property on a profitable basis. From this time forward the operation of this property was continuously successful.

In connection with the underground development that he carried forward, Mr. Rohn studied smelting with particular regard to the require-

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<sup>1</sup> See U. S. Geol. Surv. 20th *Annual Report*.

<sup>2</sup> See U. S. Geol. Surv. 21st *Annual Report*.

ments of the Pittsmont mine ores and rebuilt the smelting plant according to the best practice then known, so that it was possible to treat ores more economically than they could have been treated in custom smelters.

In the year 1909, through Mr. Rohn's efforts, the Pittsmont property was absorbed by the East Butte Copper Mining Co.; the consolidated East Butte properties rapidly becoming important producers of copper, retiring the original Pittsmont indebtedness from earnings and going on a dividend basis in 1917. Production of this company from its own and some custom ores has ranged from 10,000,000 to 25,000,000 lb. of copper per year.

Mr. Rohn was an automobile enthusiast, and about 1913-15, he was deeply interested in road building, particularly roads running out of Butte. As president of the Silver Bow Roads Assn., chairman of the Montana State Highway Commission, and also as an independent contractor, Mr. Rohn left a permanent monument to himself in the building of several hundred miles of good roads in the territory surrounding Butte.

While at Butte, Mr. Rohn was active in community projects. He was an organizer of the Butte Chamber of Commerce; a member of the Executive Committee of the Butte Employers Assn.; a member of the Executive Committee of the Montana State School of Mines; a director of the Silver Bow and Butte Country Club, and active in other representative organizations. He belonged to the American Institute of Mining and Metallurgical Engineers, Mining and Metallurgical Society of America, and Lake Superior Mining Institute.

As the problems in connection with mine and reduction plant at Butte became largely solved, Mr. Rohn became interested in the development of the oil industry in the Rocky Mountain States. In 1919, he moved to Denver, where he made his home for the remainder of his life.

On Sept. 19, 1923, he visited Butte to examine a newly equipped shaft of the Pittsmont mine. Standing on a scaffolding, with others of the operating force, he was having the skip run from the shaft into the dumping cradle and back again. He leaned forward, presumably to see more closely the operation of the skip as it dropped back into the shaft from the dumping cradle, and the top of his head was caught between the skip bonnet and the edge of the ore bin. He was killed instantly.

Mr. Rohn is survived by his widow, Mrs. Lou Foster Rohn; by a son, James, attending the Golden School of Mines in Colorado; and by his mother, Mrs. Jane Rohn of West Bend, Wis., three brothers and one sister.

The regard in which he was held by his close associates cannot be better expressed than by the following tribute offered as a memorial in booklet form by the employees of the East Butte Co. and bearing the name of every employee of that organization.

"In the race men run some do outstrip their fellows—some achieve wealth, some fame, but he achieves most who wins the respect, confidence, and regard of his fellow men.

"Death has ended the race for one who has so achieved, his smile is forever stilled, his kindly counsel will no more be heard. Yet, so well did he run the race, so well did he meet his stewardship, so deeply did he enter the hearts of his fellow workers that forevermore will his memory be cherished.

"Such is our simple tribute to the man we knew and loved."

J. H. WARNER.

#### AS A GEOLOGIST

It was my privilege to know Oscar Rohn from the time we began our geologic training together under Van Hise—in the lecture room and in field trips to the Lake Superior country. Rohn's first field work was in the Lake Superior region where he took up a number of problems relating to the iron ranges and to the Keweenaw lava flows of the north shore of Lake Superior, his graduating thesis being on the Beaver Bay diabase. In connection with these investigations he made up, with prodigious labor, a systematic set of Lake Superior rocks to illustrate some of the special features covered in the United States Geological Survey monographs. This collection, known as the Rohn Collection, was widely distributed in universities and museums all over the world. His attack on the problem of Lake Superior geology was a vigorous one, and large results would certainly have come if he had been permitted to continue in this field. He next went to Alaska for two seasons with the United States Geological Survey, and for the time became very much interested in the study of glaciers and other Alaskan problems. He not only made many new observations, but laid out a plan for a systematic study of glaciers which, if followed through, would have been of the widest scientific import. On his return from Alaska, Rohn took charge of an important iron-mining operation in the Lake Superior country. By vigorous exploration, he largely increased the holdings of his company, and these were in time absorbed by the United States Steel Corporation.

With the absorption of his company by another interest, Rohn went west and, after considerable activity in the Nevada gold fields, undertook the development of the East Butte property. This was his dominant interest to the time of his death, though in later years he gave considerable attention to oil exploration and development of new properties in Montana, Colorado, and elsewhere. During this period he was responsible for the initiation of much investigative work of value, such as the study of wall-rock alterations in the East Butte veins by W. J. Mead and C. T. Kirk. He was always alert to the possibilities of encouraging such work, not only for their immediate commercial bearing, but in the interest of advancement of the science of geology.

C. K. LEITH.

## Albert Ladd Colby

ALBERT LADD COLBY, who died suddenly of influenza at Torquay, England, on Apr. 30, 1924, was born in New York City, on June 26, 1860. He was educated in the public schools of New York, at the College of the City of New York, and received the degree of Ph. B. from the Columbia School of Mines in 1881. He continued his studies at Columbia, acting occasionally as assistant to Prof. C. F. Chandler, until 1883. For the next three years he was Assistant Professor of Chemistry in Lehigh University; then head chemist and metallurgical engineer of the Bethlehem Steel Co., at Bethlehem, Pa., occupying the latter position until 1903. As head chemist his active and inventive mind devised several improvements in apparatus for increasing the rapidity and accuracy of the analytical work; as metallurgical engineer, he was, from time to time, in charge of the blast-furnace, open-hearth, bessemer, and puddling departments; he had entire charge of the inspection, assignment, and economic use of all metallurgical materials, and he early gave his attention to the formulation of specifications for metallurgical materials—an activity in which he long held a distinguished part in this country, and as a representative of his own country in England and Europe. He also served as expert for his company in patent suits, again laying the foundation for valuable service later as a consulting engineer. In this latter capacity he was excelled by few, if any, contemporaries in the iron and steel industry. His mind was ingenious, thorough, clear, and keen, both in the preparation of evidence and its presentation to the Court. He very quickly appraised the value of evidence, or of an answer to a question, and knew how to secure the information, either from the available literature of any language, or by special researches or plant studies. In the executive control of literary research for patent purposes, his long training, infinite capacity for digging through long series of articles in English, German or French, and clear formulation of the vital subject matter for the guidance of assistants, made him invaluable. He was also an adept in collecting information on special branches of his profession. For example, when the science of metallography began to assume importance, he made the first really comprehensive bibliography covering the literature of all siderurgical countries; for the newly formed International Nickel Co. he gathered all the information extant on the subject of nickel steel, both in the literature and in the minds of experts in America and Europe. Two books testify to the thoroughness of his work in this capacity, viz.: "American Standard Specifications for Steel,"

1902, and "Reinforced Concrete in Europe," 1909, besides many monographs.

On the completion of his work for the International Nickel Co., Mr. Colby practiced as consulting engineer, with office in New York, and later in Bethlehem, although he always maintained a branch office in New York City. He practiced a good deal in Europe, representing American firms and inventors there, which his familiarity with French and German and wide acquaintance among the prominent iron and steel men especially fitted him to do. While connected with the Bethlehem Steel Co., from the year 1886, he was in demand by other companies as consulting engineer or expert in patent suits. In 1906, he began to specialize in byproduct coke manufacture, and practiced in this industry for several years.

Mr. Colby will be remembered particularly for his life-long work on the specifications of steel, for his contributions to the advance of metallurgical knowledge in his several compilations of specialized information, for his public work as a representative of the industry, and for his active and disinterested support of technical societies. In 1900, he represented his company at the Paris Exposition, and served as Juror in Metallurgy and official representative of the American Association of Steel Manufacturers; he was also U. S. representative at the International Congress for Testing Materials of Construction. He was Special Iron and Steel Commissioner in the Department of Mines and Metallurgy at the St. Louis Exposition, 1904, and, during the late war, took an active part in the standardization of aircraft steels. He was Secretary of the American Association of Steel Manufacturers, which, during his incumbency (1897 to 1905), made the first successful effort to standardize specifications for finished steel, and he served actively on committees of the American Association for Testing Materials, and its international associate, in formulating steel specifications. Space does not permit our listing all the committees on which he served in his various technical societies, which included: the Iron and Steel Institute of Great Britain, American Society of Mechanical Engineers, American Institute of Mining and Metallurgical Engineers, American Chemical Society, American Society of Civil Engineers, Society of Chemical Industry, American Iron and Steel Institute, Franklin Institute, German Iron and Steel Institute, American Foundry-men's Association, Engineers' Society of Western Pennsylvania.

On June 20, 1894, Mr. Colby married Miss Agnes Wilson Lee, of Lewistown, Pa., who, with their two children, survives him.

BRADLEY STOUGHTON.

## Chester Wells Purington

CHESTER WELLS PURINGTON was killed at Yokohama on Sept. 1, 1923, in the Japanese earthquake. Mr. Purington was born in Boston, Mass., Oct. 27, 1871. He prepared for his entrance to Harvard at the Boston Latin School and graduated from Harvard in the class of '93.



CHESTER WELLS PURINGTON.

He started out soon thereafter investigating gold deposits of the Appalachian system in the South and in 1895, made a trip to Alaska, investigating the gold deposits of that territory. The summer and fall of 1896 found him in the San Juan country of Colorado examining the gold and silver properties in the Telluride and Rico districts and in the La Plata Mountains. In the meantime, he had served on the economic staff of the U. S



Geological Survey as assistant to the late Geo. F. Becker. He spent most of 1897 in Europe, traveling through Belgium, Germany, Russia, Holland, Austria, and Switzerland, when he became deeply impressed with the possibilities of Russia, and made several examinations of gold, iron, and copper deposits in the Ural Mountains.

For the next two years, Mr. Purington was engaged in professional examinations in South America and in various parts of the United States. In 1900, he devoted his efforts to practical mining, first at a hydraulic mine in southern Oregon and then at the famous Camp Bird mine in Colorado.

From 1902 to 1907, Mr. Purington was consulting engineer in Denver, in partnership with Godfrey Doveton; he also had an office at 20 Copthall Ave., London. In 1904, he prepared a special report on costs of placer mining in Alaska, which was published by the U. S. Geological Survey. This was followed by many examinations in Colorado, Arizona, Idaho, Wyoming, Utah, and Mexico, where he examined the Cananea Consolidated. In 1907, he made investigations in far eastern Siberia for British companies, including the property of the Orsk Goldfields, Ltd., of London. This property was located on the Amur River about 60 miles west of Nikolaievsk. Here he proved a large area of dredging ground, which was afterwards equipped with two American dredges which operated successfully for many years under his direct control and management.

The year 1911 found Mr. Purington in Alaska examining the property of the Pioneer Mining Co. at Nome; he then returned to Russia, making many examinations in various parts of that great mining country. Impressed with the many difficulties encountered in handling frozen gravel, he studied this subject and applied the results to many improvements in the Lenskoi mines, in the Irkutsk Province of Siberia. All of this work was done while he was consulting engineer for the Lena Goldfields, Ltd., of London, who owned a controlling interest in the Lenskoi gold mines.

With several associates he organized the American Committee of Engineers in London in connection with the conduct of the war. This committee had about one hundred members and acted as a technical clearing house of ideas in assisting the Allied governments. It dealt with Russian military transport at the front, anti-submarine devices, aeronautics and Allied propaganda for Russia. This committee also furnished information to the United States Consulate in London, the Council of National Defense in Washington, and gave much aid to our government during the war. In 1918, Mr. Purington served with the Military Intelligence Staff in Washington, and also in the service of the United States Bureau of Mines in England and at Paris in the preparation of special reports; on March 10, 1923, he was appointed Major in the

Officers Reserve Corps of the United States, in recognition of his service to this country during the war.

At the close of the war, he returned to Siberia and obtained large concessions of placer property on Okhotsk Sea on the Pacific Coast of Siberia. As that district was in the zone of revolutions and civil war, many difficulties were experienced. He was very enthusiastic about the wonderfully rich placer deposits existing for many miles on the rough seacoast of the Okhotsk, and during the last three years he made many trips to inspect these properties and investigate the many mines, which were operating with primitive hand methods.

Because of the unsettled political conditions on the Siberian coast, Mr. Purington was obliged to postpone many activities in that section and therefore had been concentrating his energies on work in the Japanese Empire, making his home in Yokohama.

Mr. Purington's writings, covering the broad field of his experiences, are well known to most of the profession and his opinions were held in the highest regard by all who sought them. Few American engineers were as well known throughout the world and as highly regarded as he was. He was a member of the American Institute of Mining and Metallurgical Engineers, the Institute of Mining and Metallurgy of London, and of the Harvard Clubs in London, Boston and New York. He was a keen observer of all valuable details and during his extensive travels he never lost an opportunity to learn something.

A. C. LUDLUM.



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